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ENVIRONMENTAL

Mr. Robert R. Stewart, Environmental Engineer
New York State Department of Environmental Conservation
Region 1 Office
SUNY at Stony Brook
Building 40
Stony Brook, New York 11790-2356

Subject:
Evaluation of Potential Vinyl Chloride Generation During Remediation
25 Melville Park Road Site
Melville, New York

Date:
7 May 2002

Contact:
Steven Feldman

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Dear Mr. Stewart:

A draft Remedial Action Plan (RAP) for the 25 Melville Park Road Site (Site) was submitted to the New York State Department of Environmental Conservation (NYDEC) on January 24, 2002. In the draft RAP, ARCADIS proposed the use of an anaerobic in-situ reactive zone (IRZ) technology for the purpose of degrading volatile organic compound (VOC) mass and controlling the dissolved VOC plume at the Site. This letter is being submitted to the NYDEC in light of concerns that have been raised regarding the ability of the IRZ technology to effectively achieve the remedial action objectives (RAOs) set out for the Site. Specifically there is concern that the reductive dechlorination products of tetrachloroethene (PCE), particularly vinyl chloride (VC), may potentially migrate off-site at concentrations above maximum concentration limits (MCLs). Based on our experience at implementing this technology at more than 100 sites, and the site-specific geochemical conditions, we believe that this potential problem can be overcome with the proper location, management and engineering of the IRZ treatment. The following sections provide more detail regarding the Site geochemistry and VC degradation pathways. Examples of VC fate from other IRZ sites are provided along with a conceptual discussion of how the IRZ would be implemented at the Site. Complete Case Studies are also included in Attachment 1.

## Site Geochemistry

As presented in the draft RAP, an anaerobic and reducing zone is present in the shallow and intermediate groundwater in the vicinity and downgradient of the loading dock area. This reducing environment has likely developed in response to the presence of petroleum related hydrocarbons identified in non-aqueous phase liquid (NAPL) in this portion of the site. These compounds can serve as an electron donor for subsurface microbes, thereby providing the energy source necessary for the microbes to deplete dissolved oxygen and utilize alternate electron acceptors. The presence of petroleum hydrocarbons has likely created the reducing environments necessary to result in the observed degradation of the PCE and TCE through cometabolic processes.

Downgradient of these reducing environments, the groundwater recovers to its more natural aerobic state. In both the shallow and intermediate zones, the levels of dissolved oxygen range from 1 to 7 mg/L. This aerobic area extends southward and off site from a zone beginning immediately south of MW-10 in the shallow zone groundwater, and encompasses MW-3, MW-4 and MW-29. In the intermediate zone the aerobic environment extends southward and off-site from MW-28D. Nitrates are also detected in this environment, which is further evidence of the existence of an aerobic and oxidizing fringe present in the downgradient portion of the site. This is significant, since the less chlorinated daughter products (such as VC) are much more rapidly degraded in aerobic and oxidizing environments. This is evidenced by the lack of VC detected in any of the downgradient monitoring wells.

## IRZ Layout

The presence of an aerobic fringe at the site provides natural controls that can be used in conjunction with the upgradient IRZ treatment lines to provide complete containment of the chlorinated VOCs on the Site. The IRZ configuration will require injecting carbon substrates into the locations where elevated concentrations of both PCE and TCE have been detected at mg/L levels. Both PCE and TCE are recalcitrant in aerobic environments, but within the IRZ where a highly anaerobic and reducing environment has been created, the half-lives for these compounds can be reduced to 15 to 30 days. The draft RAP proposes an IRZ treatment line for the shallow zone groundwater near MW-12, and for the intermediate zone in the vicinity of IW-10. Pending the initial results of the IRZ, an additional treatment line in both the shallow and intermediate zones may be proposed for the area near MW-7 (shallow) and MW-27D (intermediate).

The approximately 60 to 90 feet of downgradient aerobic "buffer zone" that currently exists at the site will be used to monitor the results of the IRZ (including polishing any VC), and the data will be used to adjust the reagent injections to achieve complete treatment.

## Case Studies of IRZ Treatment

Several Case Studies of ongoing IRZ treatment projects were reviewed to compile information on the relationship between inducing the reductive dechlorination of source type VOCs (e.g., PCE and TCE) and the presence of VC in groundwater. Several charts depicting VC fate are provided in the text, and Case Studies are included in Attachment 1. A summary of the Case Studies or projects referenced in this letter is provided below.

- **Site 1.** This site is a former plating facility located in the San Francisco Bay Area. A full-scale in situ anaerobic treatment approach was initiated at the site in 1997. Three site wide injection events consisting of a mixture of molasses, water and supernatant (as an innoculant) were implemented over a three-year period. Hexavalent chromium concentrations were reduced from an average maximum of 80 mg/L to less then 0.050 mg/L over the treatment time period. Similarly, TCE and other chlorinated solvents were reduced from an average maximum of 3 mg/L to the method detection limit (0.010 mg/L). This site received a no further action (NFA) letter from the California Water Quality Control Board in 2000. A copy of the NFA is included in the attachments.

- **Site 2.** Site 2 is a Superfund site located in Central Pennsylvania. An automated full-scale anaerobic injection program was utilized at the site to treat hexavalent chromium and TCE present in groundwater (in lieu of a pump and treat system).

- **Site 3.** Site 3 is located in the Newark Basin in north-central New Jersey and shows the results of a pilot and early full-scale treatment in the middle of a 3,000 foot long PCE plume in bedrock. Results from this pilot show ppm levels of PCE completely removed, as evidenced by the elevated levels of ethene created in the treatment zone. These results were accepted by the NJDEP and a larger scale system was deployed at the site. Most of the extraction wells previously used to contain the plume and remove mass have been replaced with IRZ treatment lines.

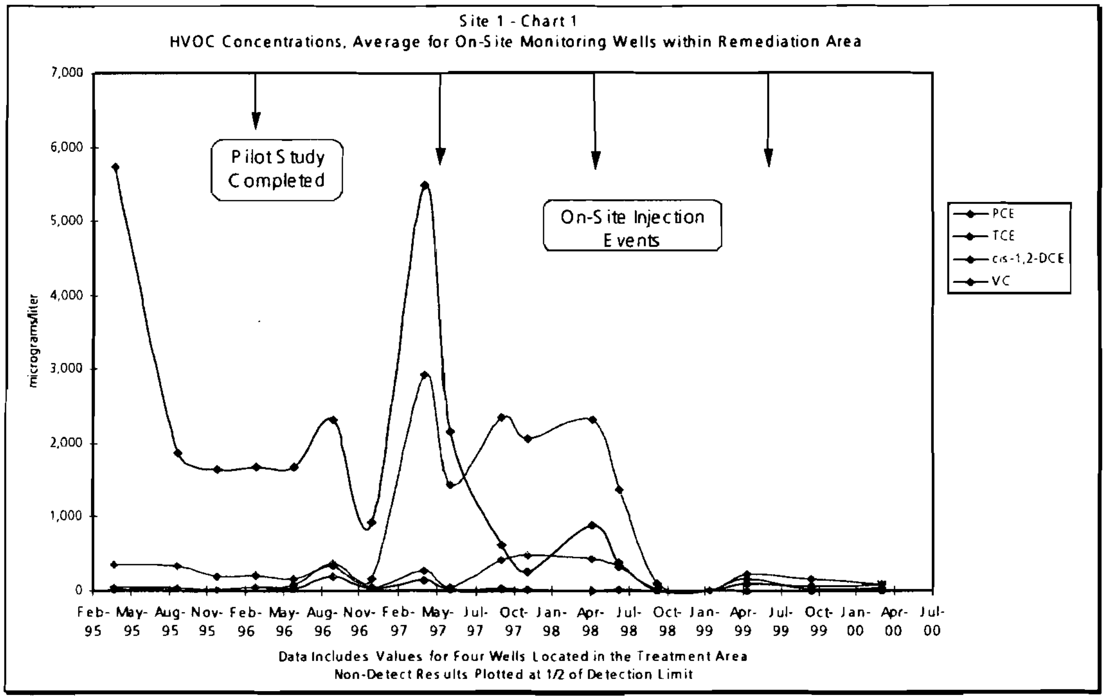
- **Site 4.** This Case Study describes an automated anaerobic treatment system installed beneath an active manufacturing facility located in London, England. Full-scale treatment employed over a two-year period has reduced maximum TCE concentrations of 22 mg/L in groundwater to a maximum of 0.014 mg/L post treatment. Some accumulation of less chlorinated daughter products are observed in the downgradient treatment area due to the presence of both floating and smear zone LNAPLs (the petroleum hydrocarbon acts as an electron donor similar to molasses and prevents the geochemical environment from equilibrating to its natural aerobic state). Pending future observations, a contingency consisting of aerobic treatment may be applied to this downgradient zone.

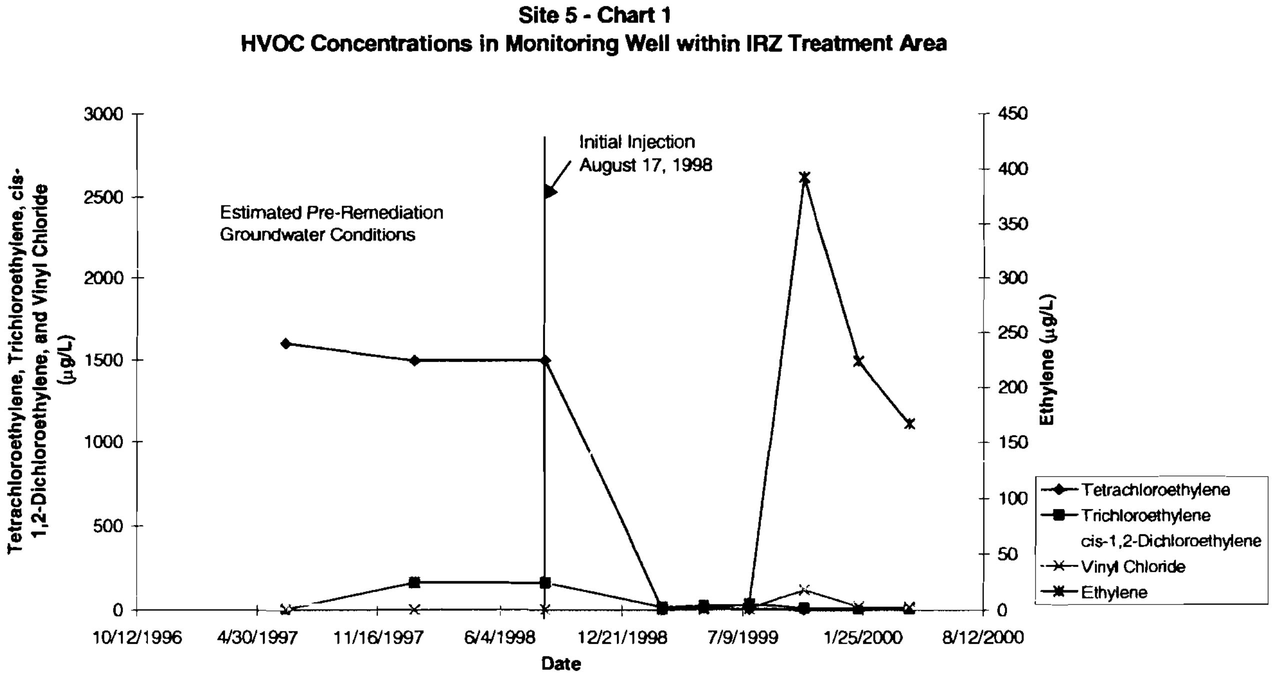
- **Site 5.** This Case Study is an example of an IRZ treatment employed in a brownfields scenario (former dry cleaner in Wisconsin) in order to foster sale and redevelopment of the property. The anaerobic treatment was completed in a two-year timeframe. PCE concentrations were reduced from low mg/L levels, and ethene was produced in the treatment area at similarly elevated levels, thereby indicating complete treatment of the source.

- **Site 6.** A pilot test IRZ treatment line was established at this site in the late 1990's on the flank of a landfill to test the efficacy of an IRZ technique in achieving containment of a mixed source chlorinated VOC plume. The results showed that the IRZ could effectively contain the plume, especially given the natural aerobic environment present in the perimeter of the landfill. Several graphs are included from the demonstration pilot test. The EPA accepted the molasses-based in situ treatment approach at this site in lieu of a 100% pump and treat method stipulated in the ROD. A copy of the ESD is also included in Attachment 1, although a complete Case Study is not included for Site 6.

- **Site 7.** A full-scale IRZ treatment is underway at a site in Wisconsin. The results from this site show how both anaerobic and aerobic degradation processes are controlling the fate of VC at this site. A figure showing groundwater remediation performance monitoring data is provided in Attachment 1.

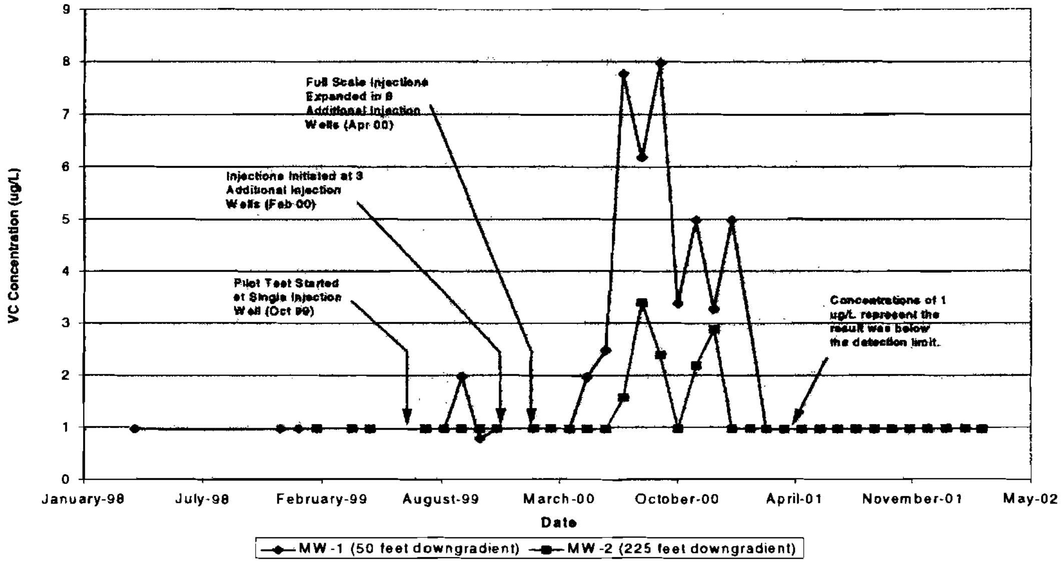
The data from these sites show several examples of the behavior of chlorinated VOCs in differing hydrogeologic, geochemical and contaminant settings. Groundwater monitoring results from the center of the treatment areas (i.e., highly anaerobic zone) show that low levels of VC may be produced during the reductive dechlorination of target PCE and/or TCE plumes. However, the levels of VC detected are generally a fraction of the initial target source solvent concentrations and are short-lived (see Site 1 - Chart 1, and Site 5 - Chart 1).


Site 1 - Chart 1
HVOC Concentrations, Average for On-Site Monitoring Wells within Remediation Area
Pilot Study Completed
On-Site Injection Events
micrograms/liter
7,000
6,000
5,000
4,000
3,000
2,000
1,000
0
PCE
TCE
cis-1,2-DCE
VC
Feb-95
May-95
Aug-95
Nov-95
Feb-96
May-96
Aug-96
Nov-96
Feb-97
May-97
Jul-97
Oct-97
Jan-98
Apr-98
Jul-98
Oct-98
Jan-99
Apr-99
Jul-99
Oct-99
Jan-00
Apr-00
Jul-00
Data Includes Values for Four Wells Located in the Treatment Area
Non-Detect Results Plotted at 1/2 of Detection Limit

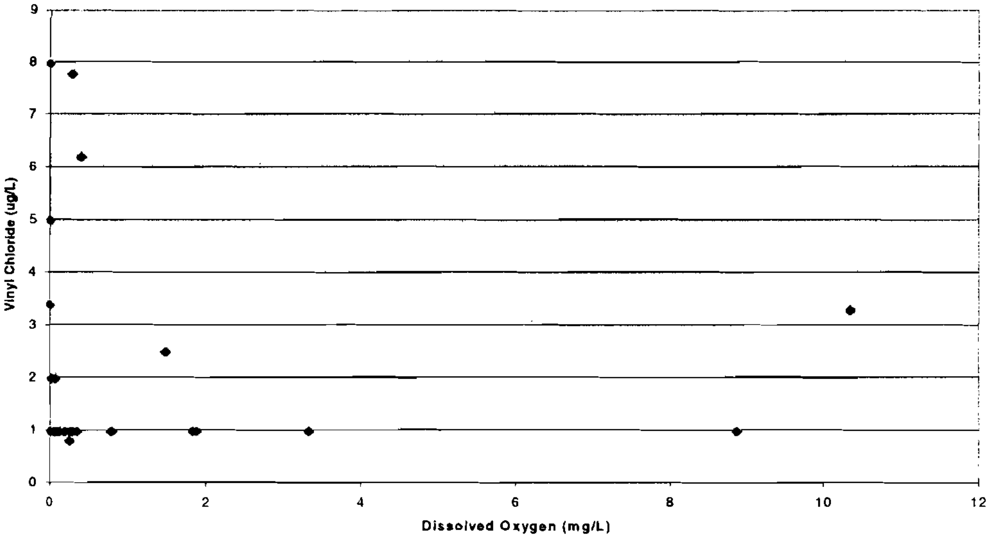

Site 5 - Chart 1
HVOC Concentrations in Monitoring Well within IRZ Treatment Area
Tetrachloroethylene, Trichloroethylene, cis-1,2-Dichloroethylene, and Vinyl Chloride (µg/L)
3000
2500
2000
1500
1000
500
0
Ethylene (µg/L)
450
400
350
300
250
200
150
100
50
0
Initial Injection August 17, 1998
Estimated Pre-Remediation Groundwater Conditions
Tetrachloroethylene
Trichloroethylene
cis-1,2-Dichloroethylene
Vinyl Chloride
Ethylene
10/12/1996
4/30/1997
11/16/1997
6/4/1998
12/21/1998
7/9/1999
1/25/2000
8/12/2000
Date

Case Studies from monitoring on the downgradient IRZ perimeter show how both aerobic and anaerobic environments can act as a control of VOC migration. Site 3 provides a Case Study where IRZ treatment of a PCE source area at concentrations of several mg/L is occurring, and monitoring wells are located 50 and 225 feet downgradient of the source area. The VC results collected from these monitoring wells through the course of the injection process show that buildup of unacceptable VC concentrations did not occur in either the anaerobic or aerobic zones (see Case Study for Site 3 and also Site 3 - Chart 1). The inverse relationship between the presence of oxygen and VC at Site 3 is shown on Charts 2 and 3.

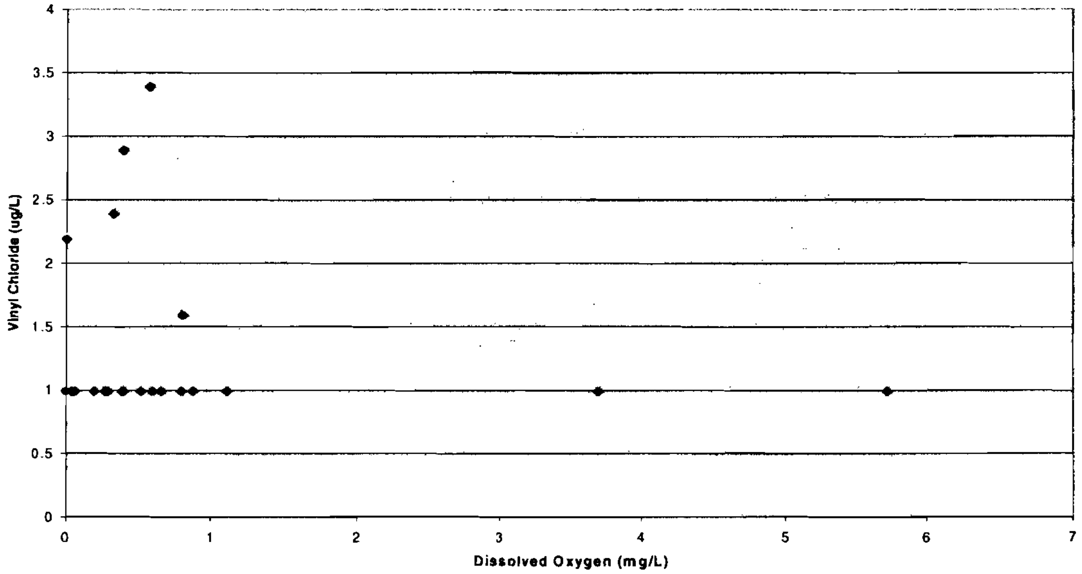
Site 3 - Chart 1
Vinyl Chloride Concentrations Downgradient of IRZ Treatment Line



Site 3 - Chart 2
Vinyl Chloride vs. Dissolved Oxygen at IRZ Perimeter Monitoring Well
(50 feet from treatment line)

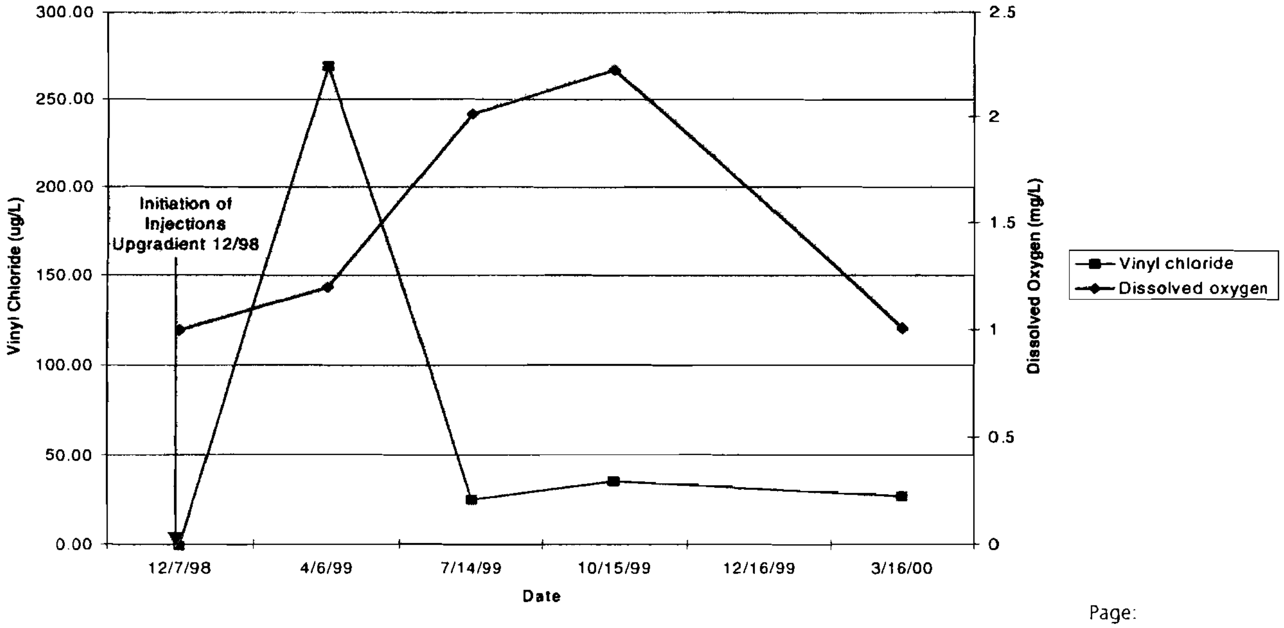


Site 3 - Chart 3
Vinyl Chloride vs. Dissolved Oxygen at IRZ Perimeter Monitoring Well
(225 feet from treatment line)

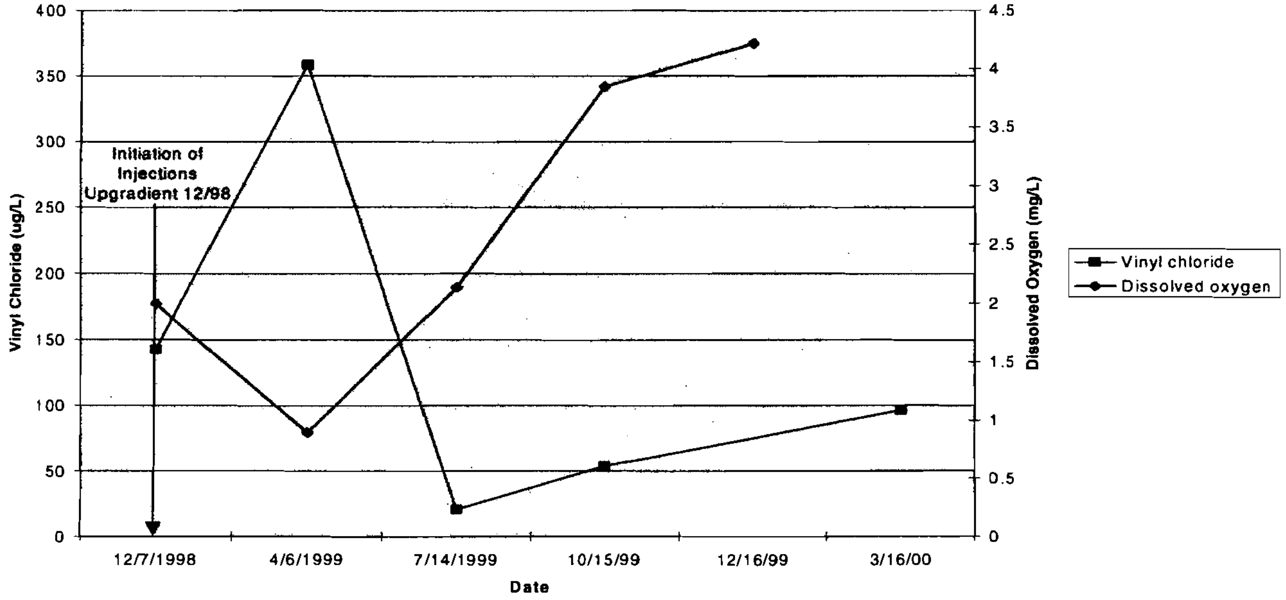


Site 6 shows the relationship between oxygen levels and VC concentrations in close proximity of IRZ injection points, where the rapid polishing of VC is achieved within 6 months (see Site 6 - Charts 1 and 2).

Site 6 - Chart 1
Vinyl Chloride and Dissolved Oxygen at IRZ Monitoring Well
(7 feet downgradient of treatment line)

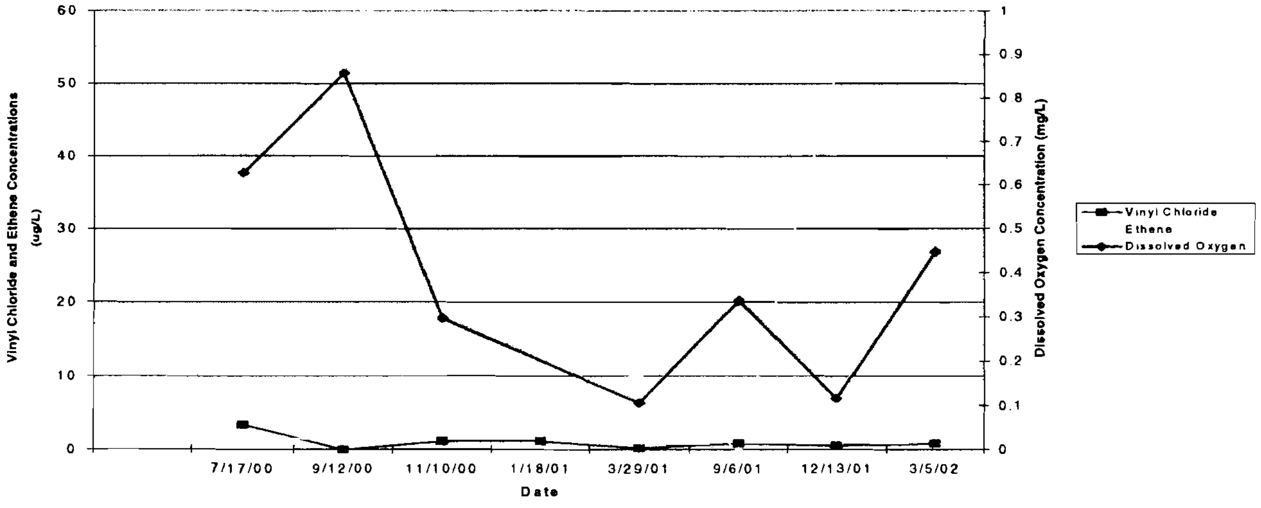


**Site 6 - Chart 2**
**Vinyl Chloride and Dissolved Oxygen at IRZ Monitoring Well**
**(12 feet downgradient of treatment line)**



Site 7 shows the results of the IRZ treatment on the fringe of the anaerobic zone, where stable concentrations of 1 to 2 ug/L of VC were detected along with the presence of approximately 50 ug/L of ethene, indicating complete treatment of the upgradient VOC mass (up to 100 mg/L of cis DCE in source area).

**Site 7 - Chart 1**
**Vinyl Chloride, Ethene, and Dissolved Oxygen in IRZ Monitoring Well**
**(30 feet downgradient of treatment area)**



## Summary of Degradation Processes

The following sections provide a detailed description of PCE and TCE degradation mechanisms that can generate VC as a daughter product and the several types of reactions that affect the fate of VC in groundwater. In contrast with the more chlorinated solvents such as PCE and TCE, the potential degradation processes for VC are numerous. These processes are described to demonstrate that the IRZ treatment program does not solely rely on the relatively slower cometabolic anaerobic processes for treatment of VC within the core of the IRZ. More rapid aerobic degradation processes usually dominate on the perimeter of most engineered IRZs and these processes provide an extra assurance that VC is not produced and transported a large distance from the treatment areas.

### Electron Acceptor Reactions (Reductive Dehalogenation)

Chlorinated compounds can be subject to anaerobic reductive dehalogenation reactions in groundwater, whereby a chlorine atom is removed and substituted with a hydrogen atom. The reductive dehalogenation mechanisms are primarily cometabolic processes that occur in anaerobic environments. Through this process, PCE is transformed to TCE, which can then be further reduced to dichloroethene, with cis-1,2 dichloroethene (DCE) the predominant isomer. Further dehalogenation reactions can produce vinyl chloride and ethene, as follows:

$$\text{PCE} \rightarrow \text{TCE} \rightarrow \text{DCE} \rightarrow \text{VC} \rightarrow \text{ethene}$$

Reductive dechlorination of chlorinated solvent compounds results in the associated accumulation of daughter products (depending upon the concentrations and relative decay rates of the parent and daughter products) and an increase in the concentration of dissolved chloride ions. In general, the more highly chlorinated compounds are most susceptible to reductive dechlorination because of their higher state of oxidation. Vinyl chloride, with only one chlorine atom, is the least susceptible of the chloroethenes to reductive dechlorination.

Reductive dechlorination has been observed at redox potentials corresponding to nitrate- and iron reducing conditions. However, the reactions are most prevalent under sulfate-reducing and methanogenic conditions. For reductive dechlorination to occur, there must be a sufficient source of carbon to support microbial growth, through cometabolism, as the chlorinated solvent compounds are used solely as an electron acceptor. At the Site, the upgradient petroleum hydrocarbon release is an example of conditions that are amenable for the cometabolic reductive dechlorination process to occur. A sufficient carbon source is present (in the form of TPH) in this part of the site and this results in bioactivity that provides the environment necessary for the strongly reducing conditions that are necessary to sustain the reductive dechlorination of the chlorinated source solvents. However, these effects are relatively localized, and aerobic conditions lacking in organic carbon are observed throughout the southern half of the site. Consequently, these are the areas that would be targeted for an IRZ application.

### Electron Donor Reactions

Under both anaerobic and aerobic conditions, lightly chlorinated compounds such as VC can be used as the primary growth substrate (electron donor) in biologically mediated oxidation-reduction reactions. More highly chlorinated solvents such as TCE and PCE are generally accepted as incapable of supporting microbial populations (Vogel 1994). For electron donor reactions, the microbial population obtains energy and organic carbon from the target chlorinated hydrocarbon (e.g., VC).

### Fate of Vinyl Chloride

An evaluation of ongoing biodegradation was conducted for the Site using the methodology presented in “Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater”, (Weidermeier et al. 1996, 1998). The protocol focuses on the presentation of data to support the hypothesis of biologically mediated oxidation-reduction (or redox) reactions. These reactions use naturally occurring microbes and electron acceptors in groundwater to mineralize halogenated organic components such as the target chlorinated solvent constituent. The ultimate reaction products are carbon dioxide, water, chloride ions and relatively innocuous daughter products such as ethene and ethane.

The biochemical reactions with respect to vinyl chloride fall into two categories:

- Relatively fast (aerobic) transformations which involve the reduction of dissolved oxygen (DO) to $CO_2$ and water ($H_2O$), and $NO_3$ to $N_2$ gas; and

- Relatively slow (anaerobic) transformations, which involve the reduction of ferric iron ($Fe^{+3}$) to ferrous iron ($Fe^{+2}$), manganese ($Mn^{+4}$) to manganese ($Mn^{+2}$), sulfate ($SO_4$) to hydrogen sulfide ($H_2S$), and $CO_2$ to methane ($CH_4$).

The first reactions to occur that utilize DO and $NO^3$ are nearly instantaneous. Once the DO and $NO^3$ are partially depleted and the environment becomes more anaerobic, the slower reactions will begin. It is worth noting that even in a reducing environment, multiple reactions occur simultaneously, including the continued reduction of oxygen, which is continually replenished by inflowing groundwater and infiltration of precipitation.

A third type of VC degradation is the anaerobic oxidation of vinyl chloride under $Fe^{+3}$ reducing conditions (Bradley and Chappelle 1996). This process uses $Fe^{+3}$ to facilitate the mineralization of VC completely to $CO_2$. This mechanism is a direct mineralization process that occurs more rapidly than the sequential dechlorination process. The rate of oxidation is clearly linked to the bioavailability of $Fe^{+3}$, but anaerobic oxidation can still take place in the presence of insoluble $Fe^{+3}$. This reaction mechanism may contribute significantly to the overall mass reduction of vinyl chloride at the Site, as indicated by the elevated levels of dissolved $Fe^{+2}$ present within the plume and the general lack of VC observed. These reactions would tend to occur at a rate slower than the pure aerobic mechanisms that rely on oxygen, but also significantly quicker than the cometabolic anaerobic degradation processes.

By calculating the concentration of electron acceptors on-site, it is possible to evaluate whether the reservoir of electron acceptors is sufficient to fully degrade VC. This calculation provides a means of evaluating Site data to determine the attenuation capacity of the geochemical environment. The chemical redox equations that control degradation of VC through the reduction of dissolved oxygen, denitrification, iron and manganese reduction, sulfanogenesis, and methanogenesis are as shown below (Weidermeier et al. 1996). The reaction for oxidation of vinyl chloride ($C_2H_3Cl$) by oxygen ($O_2$) is:

$$C_2H_3Cl + 2.5O_2 \rightarrow 2CO_2 + H_2O + H+ + Cl-$$

The reaction requires 2.5 moles of oxygen to metabolize 1 mole of vinyl chloride. On a mass basis, the ratio of oxygen to vinyl chloride is given by:

Vinyl Chloride - 2(12) + 3(1) + 35 = 62 gm

Oxygen - 2.5(32) = 80 gm

Stoichiometric mass ratio of VC to oxygen = 62/80 = 0.77:1.

This calculation shows that, in the absence of microbial cell production, 1 mg of $O^2$ leads to complete metabolization of 0.77 mg of VC. Based on this ratio, and the presence of up to 7 mg/L of oxygen that is observed along the downgradient perimeter of the site, the concentration of electron acceptors is not a limiting factor at the Site in attenuating VC. The data will be evaluated during the IRZ treatment process to ensure that a sufficient attenuation capacity is available to control VC concentrations.

A set of chemical equations can also be written for the other redox reactions that degrade VC as follows (Weidermeier et al. 1996):

Denitrification: $C_2H_3Cl + 2NO_3^- + H^+ \rightarrow 2CO_2 + 2H_2O + N_2 + Cl^-$

Iron reduction: $10Fe^{+3} + + C_2H_3Cl + 4H_2O \rightarrow 2CO_2 + 11H^+ + Cl^- + 10Fe^{+2}$

Manganese reduction: $C_2H_3Cl + 5MnO_2 + 9H^+ \rightarrow 2CO_2 + 6H_2O + 5Mn^{+2} + + Cl^-$

Sulfate reduction: $C_2H_3Cl + 1.5H^+ + 1.25SO_4 \rightarrow 2CO_2 + 1.25H_2S + H_2O + Cl^-$

Methanogenesis: $C_2H_3Cl + 1.5H_2O \rightarrow 2.25CO_2 + 3.75CH_4$

The nitrate series is characterized, in the absence of microbial cell production, by a stoichiometric mass ratio of approximately 0.5:1, the ferrous iron series by a mass ratio of approximately 0.11:1, the sulfate series by a mass ratio of approximately 0.52:1, and the methane series by a ratio of approximately 2.27:1.

In summary, the fate of VC at the Site is complex, with many different reactions that can potentially occur. Some of the environments that are amenable to the rapid degradation of VC are present at the Site in the buffer zone between the anaerobic zone and the downgradient property boundary. There are many potential mechanisms by which VC can undergo a rapid dechlorination process to carbon dioxide, water, chloride ions, and daughter products such as ethene and ethane. By ensuring that the IRZ remedy maintains an aerobic buffer space between the anaerobic reaction zone and the downgradient property boundary, we believe that there will be sufficient residence time to degrade VC that may be generated as a daughter product through the reductive dechlorination of source compounds (e.g., PCE and TCE).

Please do not hesitate to contact us if you have any questions.

Sincerely,

ARCADIS G&M, Inc.

Steven Feldman

Steven M. Feldman
Project Manager

Nicholas Valkenburg

Nicholas Valkenburg
Project Director

# ATTACHMENT 1

# SITE 1

### Site 1 – Manufacturing/Plating Facility, Northern California

ARCADIS has successfully completed an in-situ bioremediation technique involving the enhanced degradation of chlorinated aliphatic hydrocarbons and the in-situ precipitation of chromium in groundwater beneath a former manufacturing/metal plating facility located in northern California. Our patented molasses injection technology has resulted in the rapid precipitation of hexavalent chromium from the groundwater and the removal of TCE and its daughter products within a three-year time frame. This was accomplished with only three injection events over the three-year treatment period. The following sections provide background information for the facility as well as a discussion of the treatment techniques and the results obtained.

### Background

A manufacturing facility located near San Francisco released hexavalent chromium into the site groundwater as a result of historical metal-plating operations. Similarly, as a result of degreasing activities in another area of the site, TCE was also released to groundwater. The use of TCE was phased out in the early 1970's. Plating operations were phased out at the site in the mid 1990's and all of the associated equipment was dismantled and removed from the facility.

Monitoring wells were initially installed in the silts and mud that underline the site in the late 1970's. Additional wells were installed over the next 20 years. Subsequent sampling of the wells identified a hexavalent chromium and TCE plume present in the groundwater at the site. Maximum hexavalent chromium concentrations were observed at approximately 160 mg/L, while maximum TCE concentrations were observed in the 20 to 30 mg/L range. Groundwater is present in the relatively low permeability silts and mud that comprise the overburden at this site. Groundwater flow is to the northwest at a maximum seepage velocity of 60 ft/year (Figure 1, Figure 2).

### The ARCADIS Approach

ARCADIS was retained in January 1995 to address the groundwater contamination issues at the site ARCADIS proposed an in-situ technology for this site, which was accepted by the Regional Water Quality Control Board (the local California regulatory authority). A pilot study using an Enhanced Reductive Dechlorination (ERD) approach was completed in a small upgradient portion of the site in early 1996. A full-scale approach was then initiated in the spring of 1997. Ninety-one injection points were installed to 24 feet below ground surface at the site (Figure 3). Injection points were installed rapidly and at a relatively low cost using a direct push approach. Hexavalent chromium concentrations have been reduced at the site from initial concentrations in the range of 66 to 140 mg/L to concentrations of 0.5 mg/L to non- detect. In the source area TCE was reduced from approximately 18 mg/L to 2 mg/L, while in the mid plume area, TCE was reduced from approximately 30 mg/L to non-detect. Similarly, the presence of daughter products of TCE provides indication that the observed results are not a result of dilution.

### Pilot Study

ARCADIS implemented a pilot study at the site in 1995/1996 to evaluate an emerging technology as an alternative to conventional excavation and/or pump and treat approaches. This technology was the in-situ reactive zone (IRZ) technology. The pilot study consisted of injecting an organic carbon reagent into selected on-site groundwater monitoring wells and into a drive-point well. The reagent included water, simple sugars (molasses), bio-nutrients such as phosphate, and supernatant to serve as a microbial innoculant.

During the pilot study, Cr(VI) concentrations in down-gradient on-site monitoring wells decreased by greater than 99%. The decreases in concentrations were first observed two months following injection and persisted beyond six months following injection. TCE concentrations in the monitoring well down-gradient of the drive-point injection well decreased by up to 96% over the 6-month term of the pilot study. The results of the pilot study were presented to the Regional Water Quality Control Board (RWQCB) and a full-scale approach was implemented soon after.

### In-situ Reduction of Cr(VI) and Chlorinated Hydrocarbons—Theoretical Basis

Cr(VI) in groundwater is not amenable to traditional *in-situ* bioremediation techniques such as bio-sparging, bio-venting, or soil-vapor extraction. *Ex-situ* physical techniques such as pump and treat are long term, costly, and of limited effectiveness. Remediation by excavation and soils removal is also costly and fails to address the presence of Cr(VI) in groundwater.

ARCADIS developed a patented, innovative technique for the *in-situ* reduction of Cr(VI) in groundwater, known as *in-situ* bio-induced hexavalent chromium reduction. The operative principal of this technique is the development of an anaerobic, chemically reductive environment. This environment is developed by the injection of an organic carbon substrate into the vadose and saturated zones of the subsurface affected by Cr(VI). Indigenous (and sometimes) introduced bacteria mediate the development of the reductive environment. The bacteria feed on sugars in the mixture depleting available dissolved oxygen (DO) as well as the most favored electron acceptors such as nitrate. The resulting subsurface environment favors the reduction of Cr(VI) by at least two methods (Suthersan, 1997):

- Biomass develops which is able to selectively utilize the Cr(VI) as an electron acceptor, and
- Biomass develops which reduces sulfates in the subsurface environment to sulfides, which in turn react extracellularly with and reduce Cr(VI).

In the remediation process Cr(VI) is reduced to the far less toxic trivalent chromium [Cr(III)] which in turn forms relatively insoluble chromic hydroxide [$Cr(OH)_3$}. The $Cr(OH)_3$ precipitates out of the groundwater to become a permanent part of the soil matrix. At equilibrium, groundwater concentrations of $Cr(OH)_3$ can be expected to be less then 50 $\mu$g/ (Suthersan, 1997). The oxidation of Cr(III) back to Cr(VI) is highly unlikely; oxidation by DO does not occur under normal aquifer conditions and other possible oxidation reactions are likewise not favored by normal aquifer conditions (Suthersan, 1997; USEPA, 1995; USEPA, 1997).

Chlorinated hydrocarbons such as TCE can also be treated under appropriate anaerobic conditions (Suthersan, 1997). These conditions include the development or presence of a consortium of anaerobic bacteria and the presence of primary substrate(s). TCE is then reductively dechlorinated to cis 1,2 dichloroethene (DCE), vinyl chloride (VC), and finally to ethene and/or ethane. Ethene and ethane can in turn serve as primary substrates. For the chlorinated ethene series of compounds, anaerobic reductive dechlorination occurs most easily for the most oxidized species (tetrachloroethene [PCE]) and more slowly for the least oxidized species (vinyl chloride). The subsurface environment created by the addition of an organic carbon substrate is amenable to the reduction of Cr(VI) and also the reductive dechlorination of TCE.

### Injection Point installation /Injection Activities

ARCADIS contracted with a drilling contractor to install temporary injection points. The injection points are in the approximate locations indicated on Figure 3. Ninety-one temporary PVC injection points were installed to approximately 24 ft bls at accessible areas throughout the site and within the former plating building (Picture 1 and Picture 2).

ARCADIS prepared a carbohydrate mixture for injection into the temporary injection points. The proprietary mixture included water, molasses, nutrients, and supernatant from a municipal wastewater treatment Facility (a microbial innoculant). Three injection events were completed at the site between 1997 and 2000. At each injection event, approximately 150 gallons of the reagent mixture was injected into each of the injection points utilizing injection equipment designed by ARCADIS (Picture 3, Picture 4). The temporary injection points remained in place for approximately three years until the remediation was complete. The wells were then abandoned in place via pressure grouting.

## Results and Discussion

Groundwater samples were collected quarterly throughout the treatment period. Samples were collected using low flow sampling methods and a peristaltic pump. The groundwater samples have been analyzed for Cr(VI), total chromium, and halogenated hydrocarbons using USEPA approved analytical methods.

### Total and Hexavalent Chromium

The concentrations of total and hexavalent chromium detected in on-site groundwater monitoring wells decreased dramatically as a result of the IRZ. Figure 4 depicts the average concentrations for total and hexavalent chromium in on-site groundwater monitoring wells for the period beginning in February 1996 through February 1999.

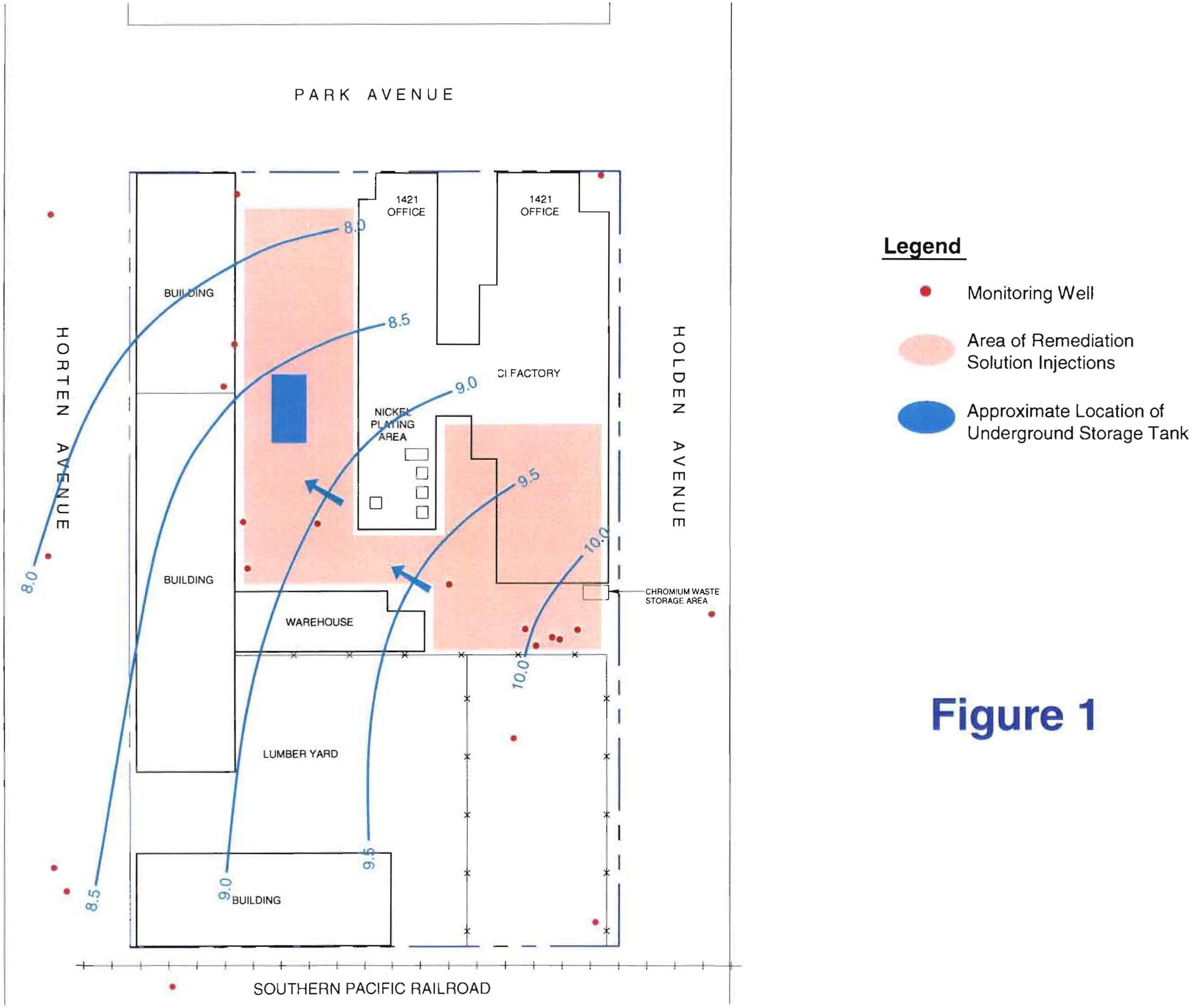
- The average concentration of total chromium in these wells has decreased by approximately 98%, from 65,670 $\mu$g/L (March 1996) to less then 500 $\mu$g/L (February 1999).
- The average concentration of hexavalent chromium in these wells has decreased by approximately 99.9%, from 74,350 $\mu$g/L (March 1996) to less then 50 $\mu$g/L (February 1999).
- Many of the on-site groundwater monitoring wells with historic concentrations in excess of 100,000 $\mu$g/L hexavalent chromium are now non-detect for hexavalent chromium. In most cases, the detection limit for these analyses is 5.0 $\mu$g/L.

### TCE

The concentrations of TCE detected in on-site groundwater monitoring wells have decreased substantially since the beginning of the remediation program. Figure 5 depicts the average concentrations for PCE, TCE, cis-1,2-DCE and VC in four on-site groundwater monitoring wells within the remediation area. These four wells are selected because historical detections of TCE in these wells have been high and because they are located down-gradient of the former TCE degreasing area at the south end of the site. Figure 6 and 7 show trends and treatment observed at two individual wells, including results obtained closer to the source where TCE was 18,000 ug/L before treatment.

- The average concentration of TCE in these wells has decreased by approximately 99% from 3,040 $\mu$g/L (April 1995) to near method detection limits (5 ug/L February 1999).
- The average concentration of PCE in these wells also decreased and is approaching method detection limits.
- The average concentration of TCE and its daughter products all showed an initial increase following the first injection event at the site. This is a desorption/surfactant effect that ARCADIS has since observed at many of our ERD sites.
- The daughter products DCE and VC reached their peak concentrations about two years after the first injection event and then lowered in the third year to concentrations near or below method detection limits.
- As a result of the full-scale ERD treatment employed at the site, the RWQCB granted No Further Action status for the facility in September 2000 (see attached letter).

# Site 1 Figures


PARK AVENUE
HORTEN AVENUE
HOLDEN AVENUE
1421 OFFICE
1421 OFFICE
CI FACTORY
NICKEL PLATING AREA
BUILDING
BUILDING
WAREHOUSE
LUMBER YARD
BUILDING
CHROMIUM WASTE STORAGE AREA
SOUTHERN PACIFIC RAILROAD
8.0
8.5
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10.0
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Legend
● Monitoring Well
Area of Remediation Solution Injections
Approximate Location of Underground Storage Tank

**Figure 1**

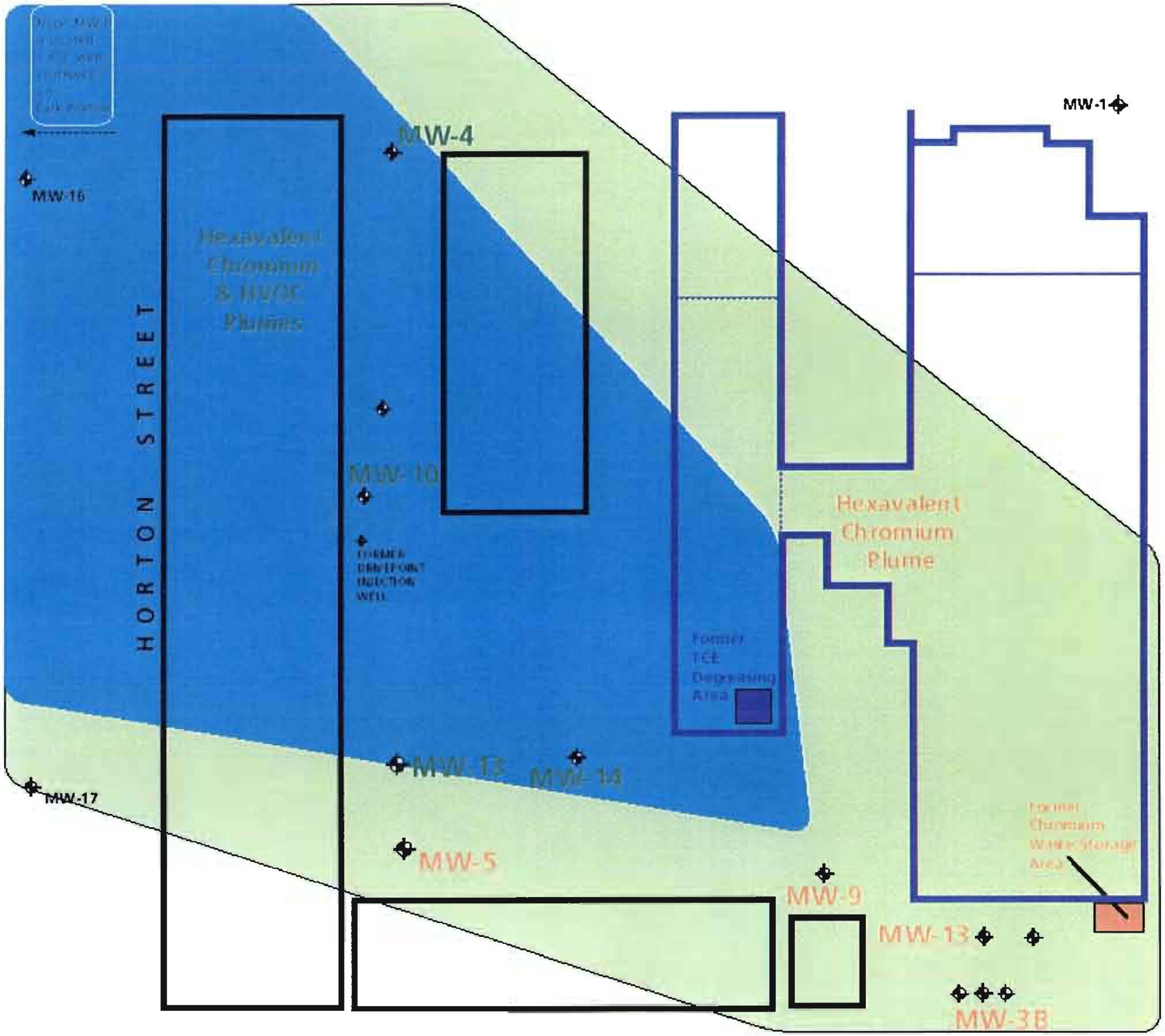

Figure 2 - General Location of CVOC/Chrome Plumes

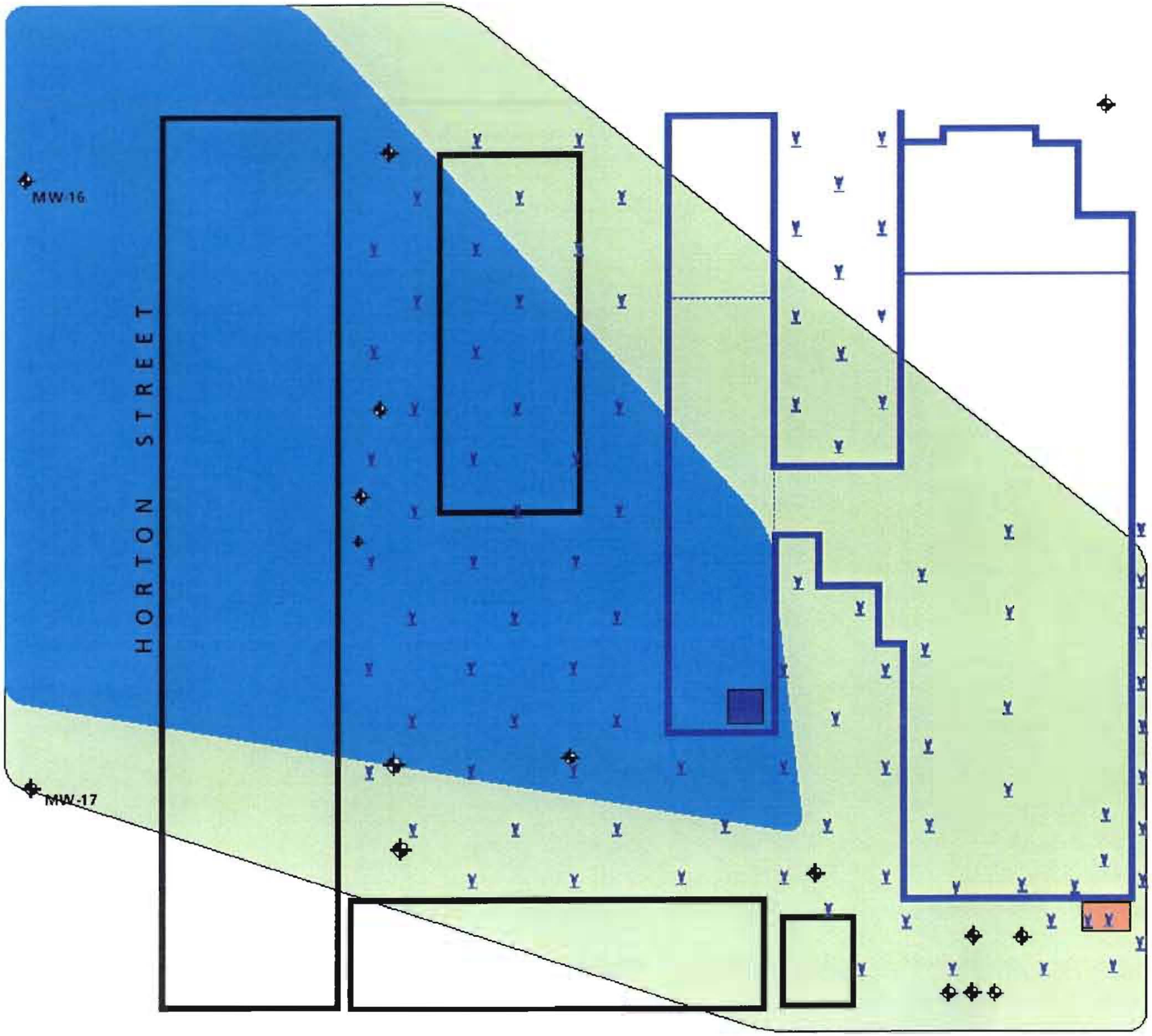

Figure 3 Location of Injection Points

Picture 1 - Injection Well Installation (inside Former Plating Building)

Picture 2 Injection Point Grid (mid plume)

Picture 3 - Mobile Injection System

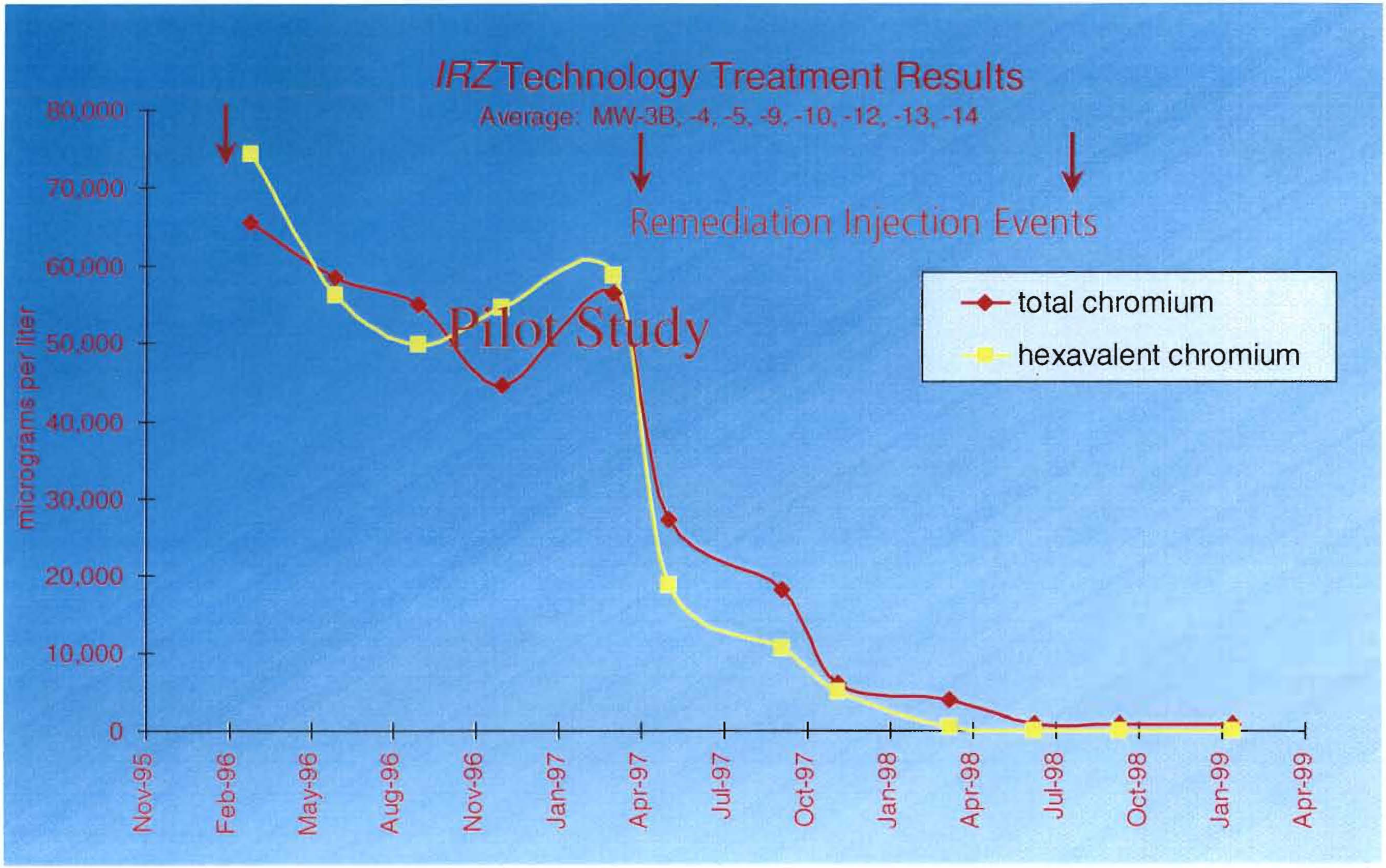

Figure 4 Average Treatment Results for Total and Hexavalent Chromium

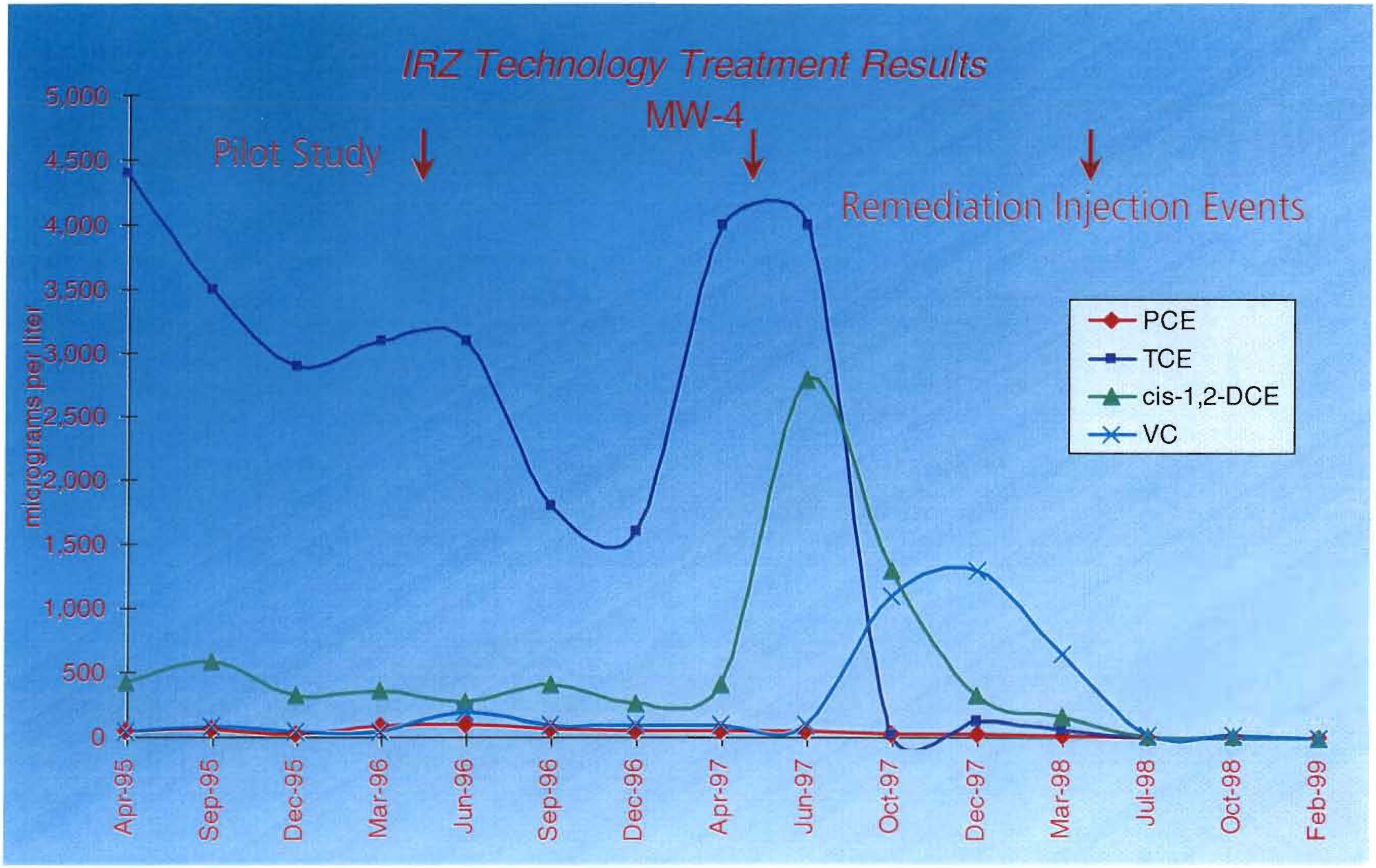

Figure 6 Treatment Results for Distal CVOC Plume

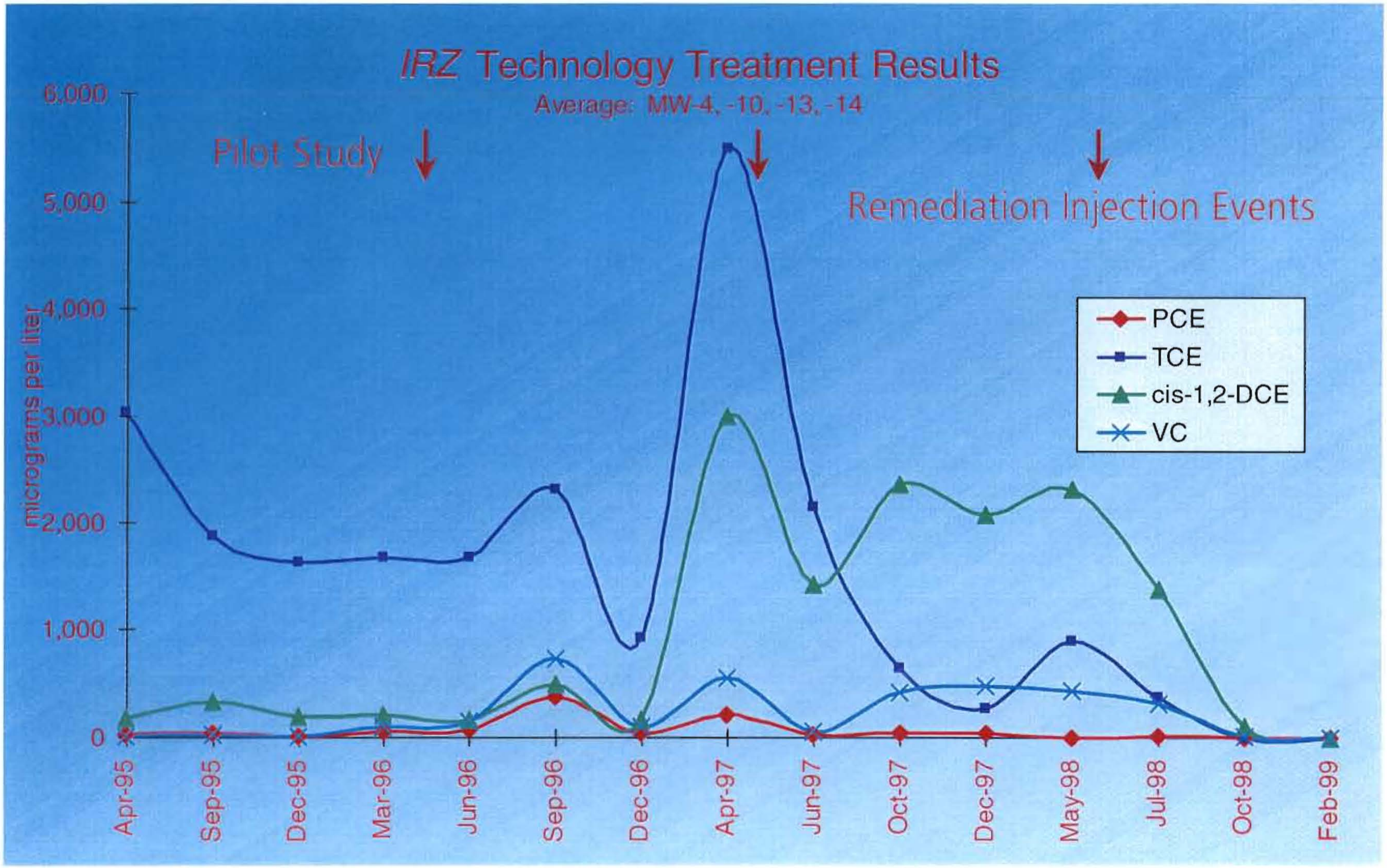

Figure 5 Average Treatment Results for CVOCs

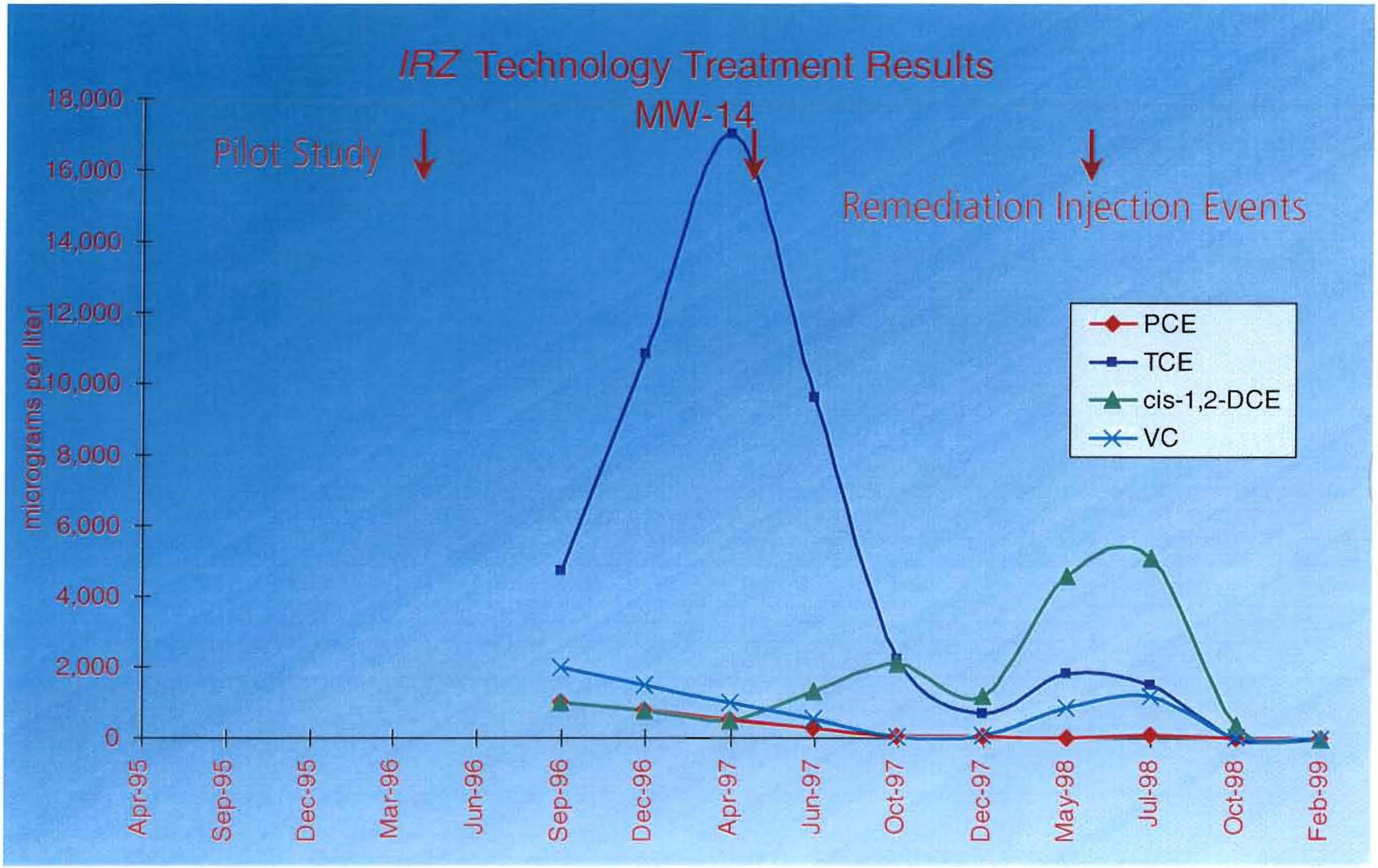

Figure 7 Treatment Results for Hot Spot Area

# California Regional Water Quality Control Board

## San Francisco Bay Region

**Winston H. Hickox**
*Secretary for Environmental Protection*

Internet Address: http://www.swrcb.ca.gov
1515 Clay Street, Suite 1400, Oakland, California 94612
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**Gray Davis**
*Governor*

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SEP 11 2000
ARCADIS Geraghty & Miller

September 7, 2000
File No. 01S0311 (MEJ)

Jeff Garvens, VP Operations
Electro-Coatings, Inc.
1401 Park Avenue
Emeryville, CA 94608

Subject: September 1, 2000 letter, Scope of Work and No Further Action, Electro-Coatings Inc., 1401 Park Avenue Parcel, Emeryville, Alameda County

Dear Mr. Garvens:

This letter responds to your letter of September 1, 2000, and grants conditional No Further Action status for the 1401 Park Avenue parcel of the Electro Coatings, Incorporated (ECI), Emeryville site, subject to acceptable completion of specific actions as proposed in your letter and summarized below and compliance with the deed restriction and site management plan. No Further Action status will allow for the sale of the property and its redevelopment into a multi-level office building and parking structure. Let it be understood that this No Further Action status applies only to the 1401 Park Avenue parcel and additional investigation and remediation will be required on the remainder of the site, including the adjacent 1421 Park Avenue parcel and downgradient offsite. As you are well aware, significant investigation and remediation has been completed on the subject parcel. Concentration of both hexavalent chrome and chlorinated solvents have dropped to below drinking water standards in most areas of the 1401 Park Avenue parcel, with the exception of the following areas: monitoring wells MW-3B, where solvents persist; and, MW-23 where hexavalent chrome was recently detected.

The Scope of Work proposed in your letter calls for installing at least three sampling/injection points within a 10' radius of both MW-3B and MW-23. These points will be first sampled for their respective pollutants and, depending on the results, injected with the reductive zone reagent which has been used for the remediation of the site. Following this, all monitoring wells and injections points will be removed from the 1401 Park Avenue parcel in preparation of its redevelopment. A new monitoring well will be installed down-gradient on the 1421 Park Avenue parcel and monitored to assure the effectiveness of this remediation. In conjunction with these remedial activities, a deed restriction and referenced site management plan will be applied to the property in order to manage the residual pollutants.

Board staff have reviewed the subject Scope of Work document and find the approach acceptable. The remedial technology used on the property has been highly successful in reducing the concentrations of both chrome and solvents in groundwater. While the proposal in the Scope of Work does not call for continued monitoring at the two specific points where elevated concentrations of pollutants persist, the proven ability of the remedial measures to reduce pollutant concentrations along with the localized area of the pollutants, provide a level of comfort that these areas no longer pose a significant threat to groundwater pollution. In addition, the proposed groundwater monitoring well down-gradient on the 1421 Park Avenue parcel is an effective method to confirm effectiveness of remedial measure in the long-term.

Based upon the acceptable completion of the activities outlined in the subject Scope of Work, available information, including the current land use, and with the provision that the information provided to this agency was accurate and representative of site conditions, No Further Action is required on the 1401 Park Avenue parcel. However, should groundwater monitoring downgradient determine that the 1401 Park Avenue parcel continues to be a source of groundwater pollution, the Board may require that additional actions be taken.

If you have any questions, please contact Mark Johnson of my staff at (510) 622-2493 [e-mail mej@rb2.swrcb.ca.gov].

Sincerely,

Lawrence P. Kolb
Acting Executive Officer

Stephen A. Hill, Chief
Toxic Cleanup Division

cc: attached list

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1131 Harbor Way Pkwy, 2nd Floor
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Richmond, CA 94804

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4665 Indian School NE
Albuquerque, NM 87110

# SITE 2

### Site 2 – Manufacturing Facility, Central Pennsylvania

In 1995 ARCADIS was retained by a Manufacturing Company to develop an alternate remedial design/remedial action (RD/RA) for a Superfund site located in Central Pennsylvania. This site contains both chromium and chlorinated solvents in the overburden groundwater. The selected remedy for the site, as described in a 1991 Record of Decision (ROD) was groundwater pump and treat. In 1995, ARCADIS developed and successfully negotiated an alternative approach for groundwater remediation with the USEPA that has saved $7,000,000 for this site in Region III. The EPA's proposed remedy included a pump and treat system that would have operated for 30 years. Our approved alternative remedy consisted of the installation and operation of an automated injection system for the in-situ precipitation of hexavalent chromium impacts present in the site groundwater. This system is also effectively remediating chlorinated volatile organic compound (VOC) impacts present in groundwater through enhanced reductive dechlorination (ERD). This alternative also eliminated the need for aboveground treatment and disposal of recovered groundwater, and since it involved active removal of the source, would significantly lower the expected treatment timeframe for this portion of the site. The ongoing remedy is removing contaminant mass at a much faster rate than the pump and treat remedy would have been able to achieve. This increased mass removal has reduced the time estimated to cleanup the site from 30 years to less than 10 years. After approximately 2 years of operation, hexavalent chromium and trichloroethene (TCE) concentrations have been reduced by approximately 70 to 90%, respectively.

A pilot study was initiated in the spring of 1995 to demonstrate the viability of the in-situ technique in precipitating hexavalent chromium from groundwater. The success of the pilot study enabled the Record of Decision (ROD) to be modified for the site to include this approach for full-scale treatment. The full-scale system consists of 20 injection wells and 16 monitoring wells. The system is fully automated and mixes and distributes a reducing reagent to the impacted groundwater area twice a day. The presence of the reducing reagent in the groundwater results in a lowering of the oxidation-reduction potential of the groundwater, thereby precipitating chromium and enabling the chlorinated VOCs to degrade via reductive dechlorination.

### Background

The 28-acre Site manufactures reciprocating aircraft engines and is adjacent to a residential neighborhood that also contains some light industry. In the mid 1980's, the local municipal water authority detected the presence of VOCs (specifically trichloroethene (TCE) and 1,2-trans-dichloroethene [DCE]), in the groundwater at a water-supply well field located approximately 3,000 feet south of the facility (Figure 1). Under instruction from the Pennsylvania Department of Environmental Protection (PADEP), groundwater samples were collected from an on-site inactive production well along with samples from other accessible wells in the area. Based on the findings, additional wells were installed at the facility. These investigations indicated that volatile organic constituents in the overburden groundwater aquifer beneath the plant were migrating from the plant in a southerly direction. Air stripping towers were installed to treat groundwater withdrawn from the municipal well field. Soon after the presence of heavy metals was also discovered within the groundwater (in particular, total and hexavalent chromium).

In the late 1980's, the EPA executed an Administrative Order of Consent for the purpose of conducting a Remedial Investigation (RI), Endangerment Assessment (EA), and Feasibility Study (FS) at this facility. In the early 1990's, the pump and treat ROD was issued for the area within the plant boundaries and soon after the EPA issued an Administrative Order (AO) to implement the remedy.

The site is underlain by unconsolidated alluvial and glacial deposits (sand, gravel, cobbles, and small boulders with relatively minor amounts of silt and clay) with a maximum thickness of approximately 37 feet. The depth to groundwater ranges from approximately 15 to 28 feet below ground surface (ft bgs). Groundwater flows primarily in a southerly direction with minor components to the southwest and southeast. A hydraulic connection between the overburden and the bedrock has been demonstrated.

Maximum total VOC concentrations in groundwater are on the order of 20,000 ug/L. The primary organic constituents of concern in the overburden aquifer are TCE and DCE. Vinyl chloride and, to a lesser extent, chromium are also present. Total chromium concentrations in groundwater are on the order of 6 milligrams per liter (mg/L).

The area targeted for in-situ metals precipitation is the western portion of the site. Prior to the six-month field design test, concentrations of total chromium (filtered) ranged from 1.65 to 5.14 mg/L and concentrations of hexavalent chromium ranged from 2.1 to 7.0 mg/L. Concentrations of cadmium (filtered) ranged from 0.0021 to 0.883 mg/L.

### The ARCADIS Approach

The in-situ approach proposed for the Central PA site is an in-situ metals precipitation approach that also acts in degrading and treating the chlorinated solvents. In-situ metals precipitation is based on the microbial reduction of hexavalent chromium to trivalent chromium, which is less toxic and less mobile than hexavalent chromium. To promote in-situ microbial reduction, a dilute molasses solution (which contains readily degradable carbohydrates) is injected into the aquifer. The carbohydrates are readily degraded by the indigenous heterotrophic microorganisms present in the aquifer. The metabolic degradation process utilizes the available dissolved oxygen contained in the groundwater, causing reducing conditions to develop. As a result, hexavalent chromium is reduced to trivalent chromium and precipitates as chromium hydroxide.

The primary reduction and precipitation mechanism of hexavalent chromium is in the form of chromium hydroxide, which has an extremely low solubility product of $10^{-31}$, which is lower than some other metallic sulfides. Resolubilization of chromium hydroxide, albeit at very low rates, will take place only at extreme pH values (less than 4.5 or greater than 10.5).

### In-situ Reduction of Cr (VI) and Chlorinated Hydrocarbons—Theoretical Basis

#### Chromium

In-situ precipitation of chromium is based on the microbial reduction of hexavalent chromium Cr (VI) to trivalent chromium Cr (III) (i.e., the oxidation state of the chromium is changed from $Cr^{+6}$ to $Cr^{+3}$). The reduction process yields significant remedial benefits because trivalent chromium Cr (III) is less toxic, less mobile, and precipitates from solution more readily than hexavalent chromium Cr (VI). The reduced trivalent chromium will precipitate as chromium hydroxide.

To promote the in-situ microbial reduction of hexavalent chromium Cr (VI) to trivalent chromium Cr (III), a dilute molasses solution (which contains readily degradable carbohydrates) is injected into the impacted aquifer via a series of injection wells. The carbohydrates, which consist mostly of sucrose, are degraded by the indigenous heterotrophic microorganisms present in the aquifer. This metabolic degradation process utilizes the available dissolved oxygen contained in the groundwater. Depletion of the available oxygen present in the groundwater causes reducing conditions to develop. As a result, the hexavalent chromium Cr (VI) is reduced to trivalent chromium Cr (III). The trivalent chromium Cr (III) then reacts with available hydroxide ions to form chromic hydroxide [Cr (OH) 3](s) precipitates. These precipitates are then retained by the soil particles within the aquifer.

#### Heavy Metals

Precipitation as sulfides is considered the dominant mechanism removing dissolved heavy metals from the groundwater, including cadmium. This technology requires a source of carbon to support microbial growth, a source of sulfate, and a population of sulfate reducing bacteria. The molasses solution will provide the source of carbon and sulfate. Sulfate reducing bacteria are normally present under natural conditions; however, in some stressed environments, the sulfate reducing bacteria may not be present. The pilot test performed at the site demonstrated that a large population of sulfate reducing bacteria may not be present at the site. To overcome the lack of naturally occurring sulfate-reducing bacteria, alternate sources of sulfate reducing microorganisms can be introduced into the aquifer. Alternate sources include: 1) filtered supernatant from an anaerobic digester and 2) sulfate reducing bacteria that are artificially cultured expressly for that purpose. Additionally, sulfide can be introduced into the aquifer in the form of sodium sulfide or calcium sulfide. The soil matrix in the aquifer will filter out precipitated metallic sulfides.

Chlorinated hydrocarbons such as TCE can also be treated under appropriate anaerobic conditions (Suthersan, 1997). These conditions include the development or presence of a consortium of anaerobic bacteria and the presence of primary substrate(s). TCE is then reductively dechlorinated to cis 1,2 dichloroethene (DCE), vinyl chloride (VC), and finally to ethene and/or ethane. Ethene and ethane can in turn serve as primary substrates. For the chlorinated ethene series of compounds, anaerobic reductive dechlorination occurs most easily for the most oxidized species (TCE and more slowly for the least oxidized species (vinyl chloride). The subsurface environment created by the addition of an organic carbon substrate is amenable to the reduction of Cr (VI) and also the reductive dechlorination of TCE.

## METALS PRECIPITATION PILOT TEST RESULTS

In August 1995, ARCADIS prepared a workplan to perform field design tests to demonstrate the effectiveness of the alternate technology and to collect data for the design of a full-scale remediation system. The Work Plan was approved by the EPA. In September 1995, molasses injection and monitoring wells were installed in the western portion of the site for the metals precipitation field design test. The metals precipitation field design test was initiated on November 21, 1995. Field measurements collected on November 30 and December 7, 1995 demonstrated a decrease in oxidation/reduction potential (Redox), indicating that reducing conditions had developed in both injection and monitoring wells (Figure 2). Decreases in dissolved oxygen (DO) were also observed in the injection wells. In addition, field measurements indicated a decrease in hexavalent chromium concentrations in both injection and monitoring wells. Results from the field test can be summarized as follows:

- Reducing conditions, as evidenced by redox and dissolved oxygen measurements, and a significant decrease in hexavalent chromium concentrations in groundwater, as evidenced by the HACH field test kit, were observed in the injection wells within 9 days after molasses injection.
- Laboratory analytical results indicate a decrease in hexavalent chromium from 2.4 mg/L to less than 0.01 mg/L in MW-3R, located approximately 5 feet from the injection wells, within approximately 70 days. In the southern area, laboratory analytical results indicate a decrease in hexavalent chromium from approximately 3 mg/L to less than 0.01 mg/L in MW-18, located approximately 12 feet from the injection wells, within approximately 155 days.

The six-month pilot test for in-situ metals precipitation was performed from November 1995 through May 1996 and the test results were submitted to the EPA in a report dated June 1996. As a result of the in-situ metals precipitation technology employed during the six-month pilot test, concentrations of hexavalent chromium decreased to below the detection levels. Concentrations of total chromium in filtered samples also generally decreased. In addition, samples adjusted for pH indicated a decrease in total and dissolved chromium with an increase in pH from 5 to 7. The results from the field test indicated that in-situ metals precipitation was a viable large-scale remedial alternative for the site. Following a review of the data collected during the in-situ metals precipitation pilot tests, the EPA requested a FFS to support an amendment to the ROD

### System Installation and Operation

During the pilot test, information necessary to design a full-scale in-situ metals precipitation system was collected. The field test indicated that individual injection wells had reactive zones ranging in width from 25 to 40 feet in a downgradient direction. A conceptualization of the full-scale system is provided on Figure 3. The components of the full-scale in-situ metals precipitation system included the following:

- a series of molasses injection wells;
- mixing tanks for molasses solution;
- pumps, piping, and associated equipment for molasses injection; and
- a programmable logic controller (PLC) to automatically control the amount of solution injected.

The full-scale system consisted of installing twenty injection wells along four treatment lines (Figure 4). Each well is constructed of four-inch PVC and installed to approximately25 ft bls. Approximately 1,200 feet of trenching was installed to connect the four treatment lines to one main distribution line. The trenches contained the piping necessary to distribute the molasses solution. One central solution feed station consisting of a heated shed, controls, and tankage was also installed at the site (see Picture 1). The shed also contained a molasses feed tank, a batch mixing tank and a solenoid distribution network to ensure that the proper volume of reagent was injected into individual wells (Picture 2; Picture 3). The reducing reagent (in this case, a mixture of edible blackstrap molasses, water and proprietary reagents) was added twice a day at low volumes (10 to 20 gallons per well), and at variable rates and concentrations (from 1:200 to 1:20 strength). The treatment system went on-line in January 1997 and monthly to quarterly sampling has been conducted since this time.

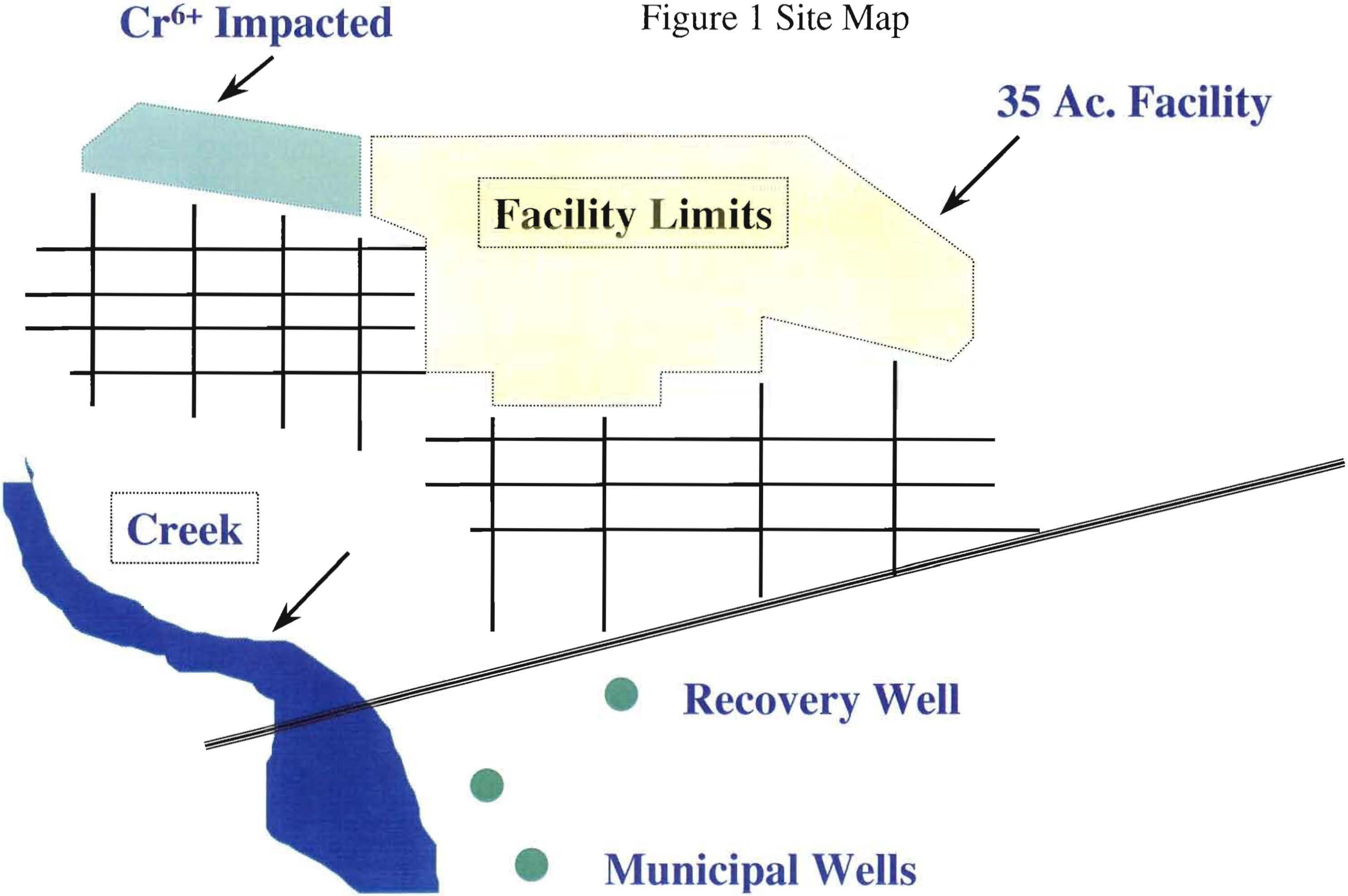
## Results and Discussion

Groundwater samples were collected quarterly throughout the treatment period. Samples were collected using low flow sampling methods and a peristaltic pump. The groundwater samples have been analyzed for Cr(VI), total chromium, and halogenated hydrocarbons using USEPA approved analytical methods.

A baseline-sampling event was conducted in January 1997 to document geochemical conditions prior to initiation of reagent injections. The baseline-sampling event indicated that anaerobic and reducing conditions were only present near the pilot injection wells (Figure 2). Prior to reagent injections, TCE was detected in four wells; however, appreciable concentrations of DCE were detected only in the two wells that exhibited an anaerobic environment.

The site initially contained maximum total chlorinated aromatic hydrocarbons (CAH) concentrations in groundwater of approximately 700 ug/L in individual wells. Data collected since the initiation of full-scale treatment from the site shows that enhanced transformation of the CAHs has resulted in significant decreases of CAHs in groundwater. Data collected after the in-situ treatment zones (or "reactive zones") were established, show significant increases in the total organic carbon content of the groundwater, in the amount of sulfide being generated by sulfate reducing bacteria, and a significant drop in the oxidation-reduction potential (ORP) of the groundwater. These reducing effects on groundwater were observed over an approximately 12,000-ft$^2$ area at the Site (Figure 5). Degradation has resulted in an observed 70% to 100% reduction in source concentrations of TCE and over a 90% reduction in observed concentrations of hexavalent chromium in groundwater. Figure 6 and 7 show the concentration trends and degradation rates achieved for the pilot and central area of the full-scale remediation system respectively. Figures 8, 9, and 10 show the effects of the full-scale system on the concentrations of hexavalent chromium plume during the first two years of operation.

Figure 1 Site Map



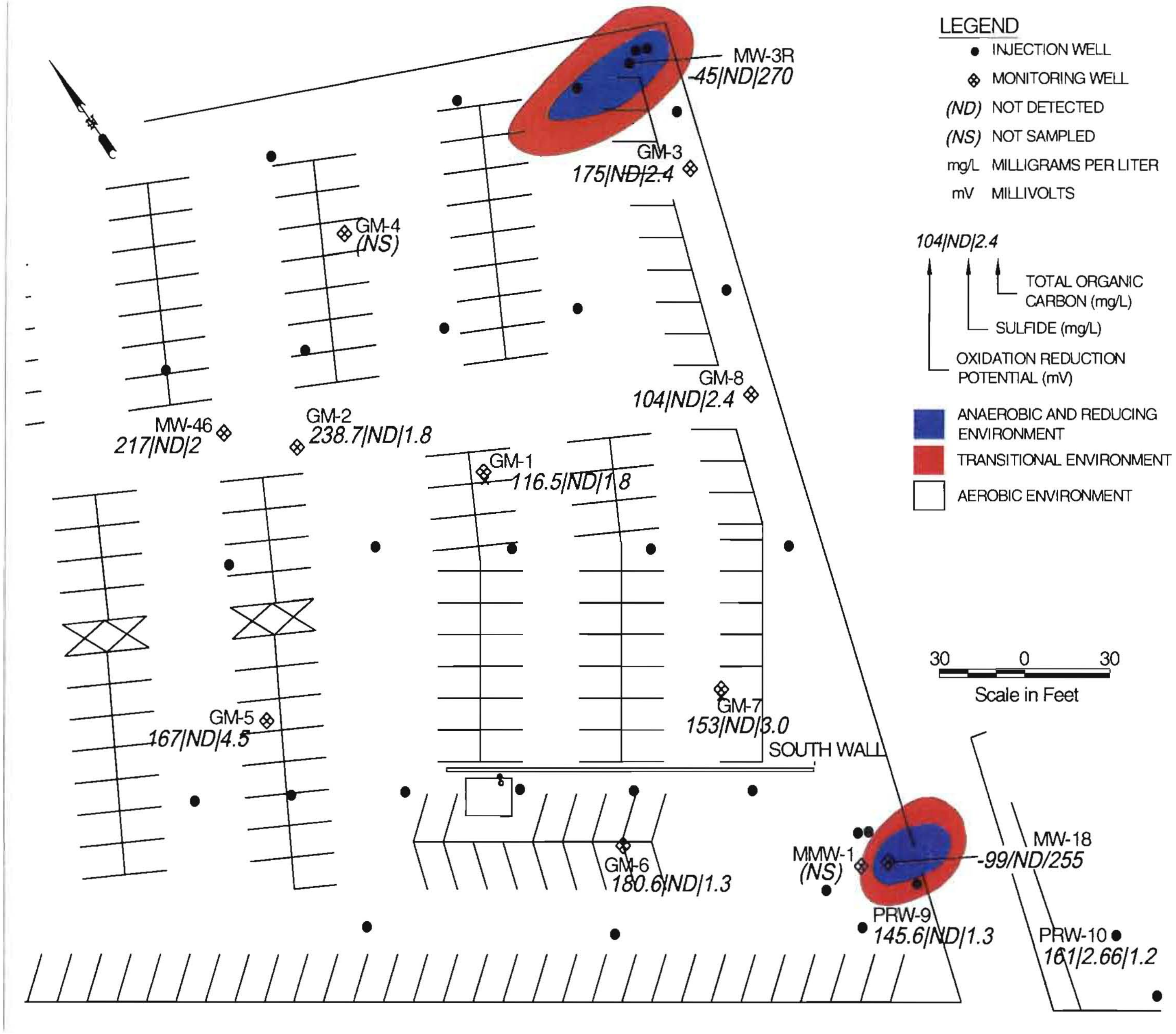


Figure 2 - Distribution of Groundwater Indicator Parameters, Baseline Conditions, January 1997

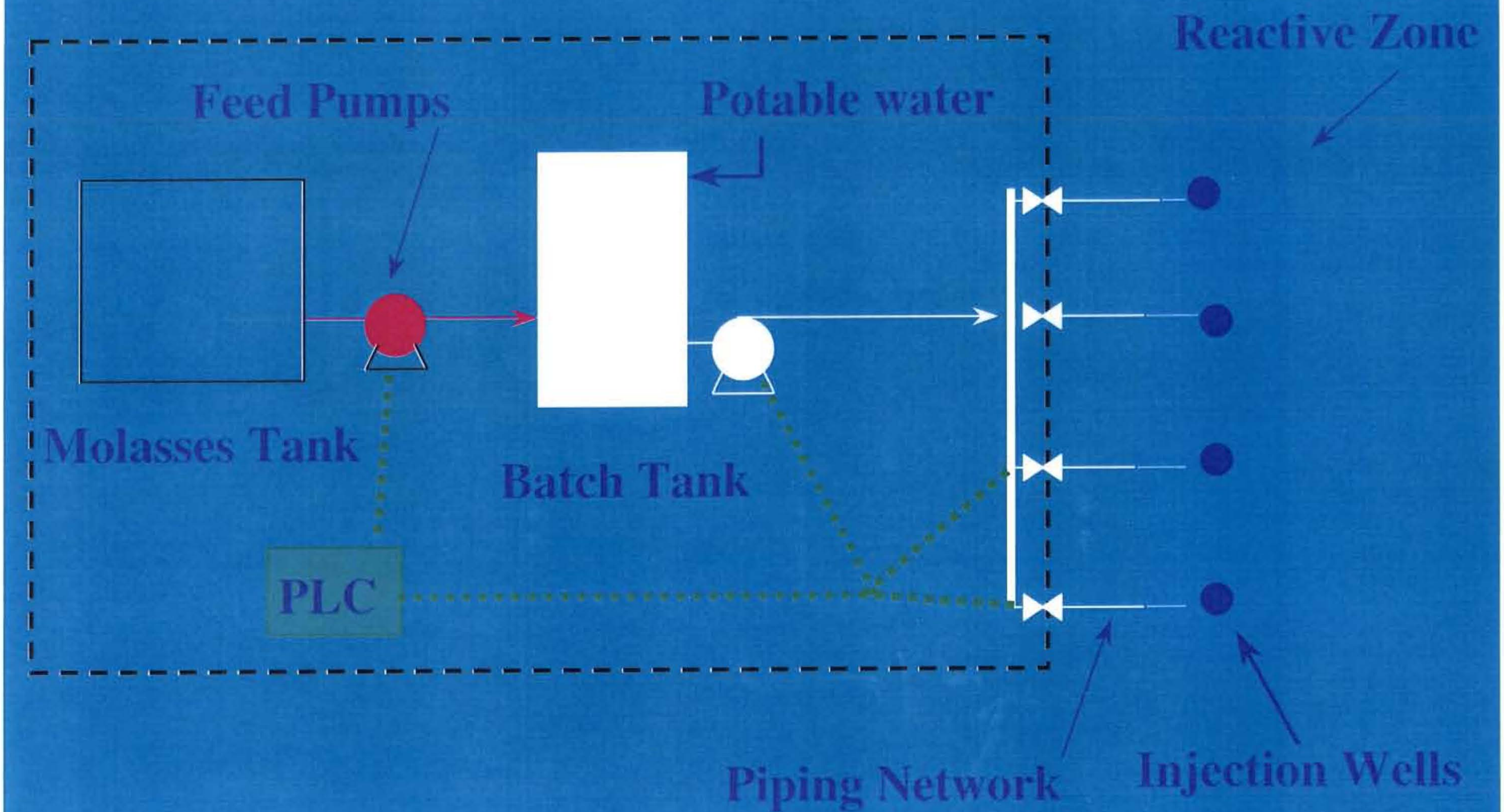
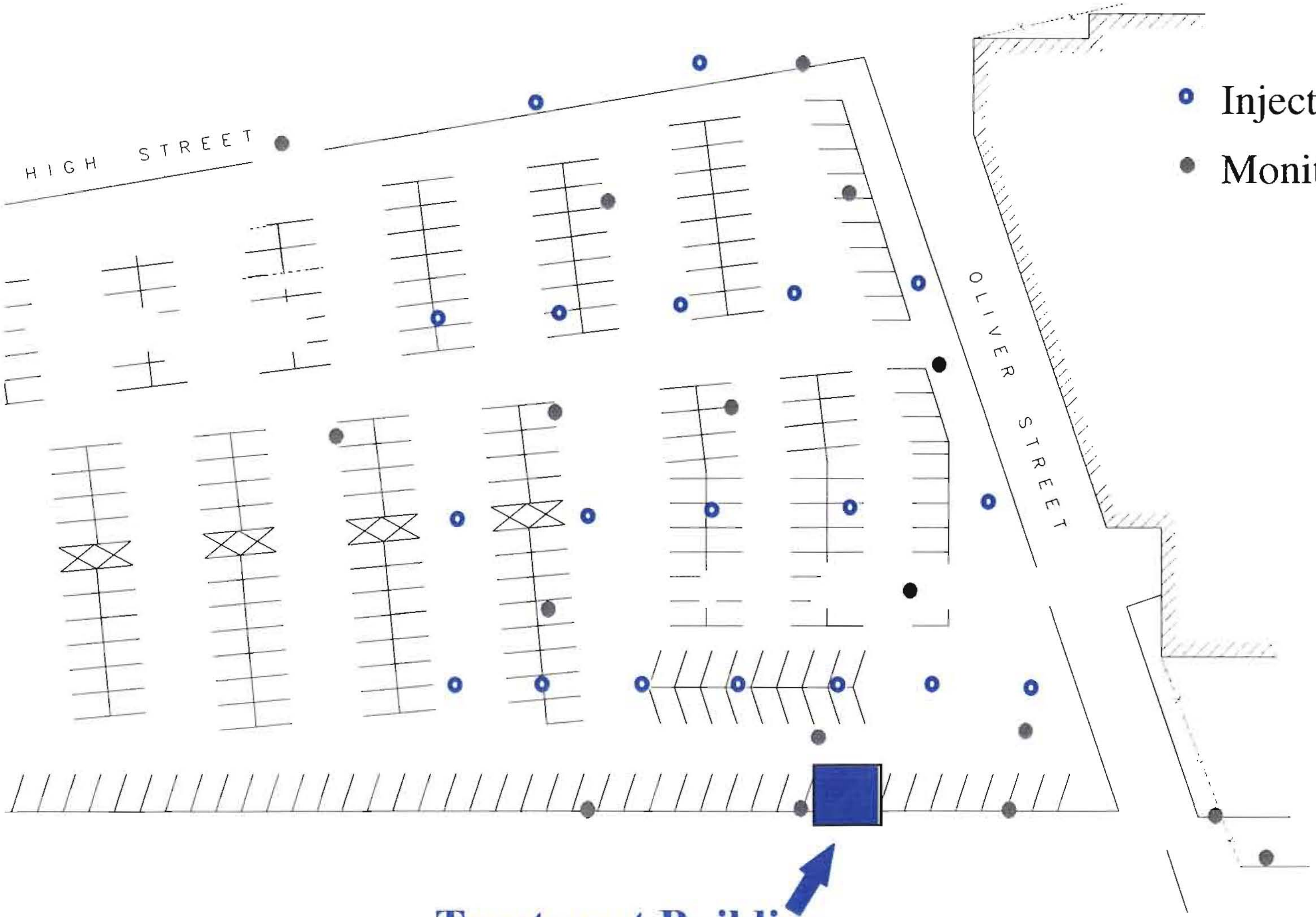


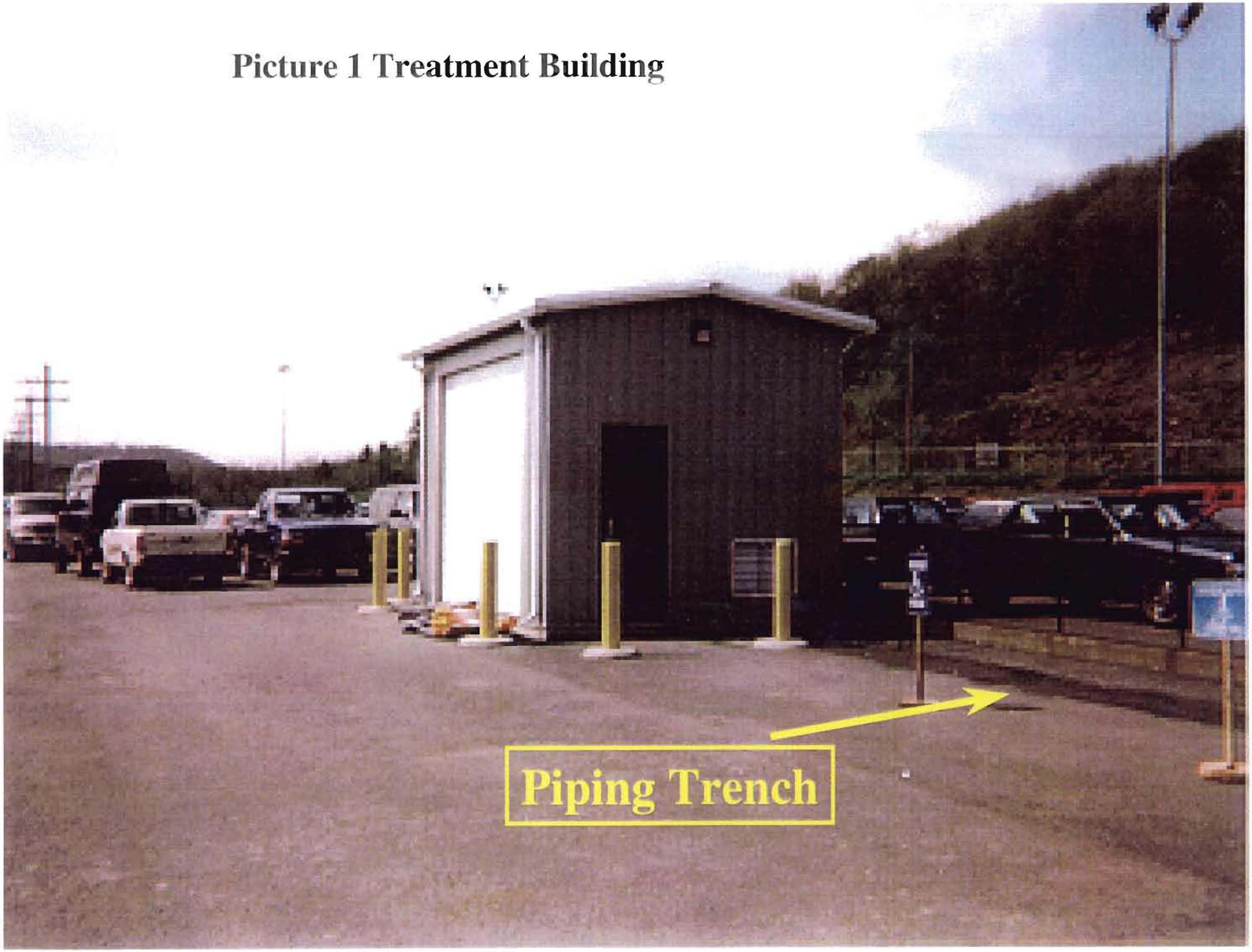
Figure 3 - Molasses Injection System Conceptual Design

# *Figure 4 Injection and Monitoring Well Network*

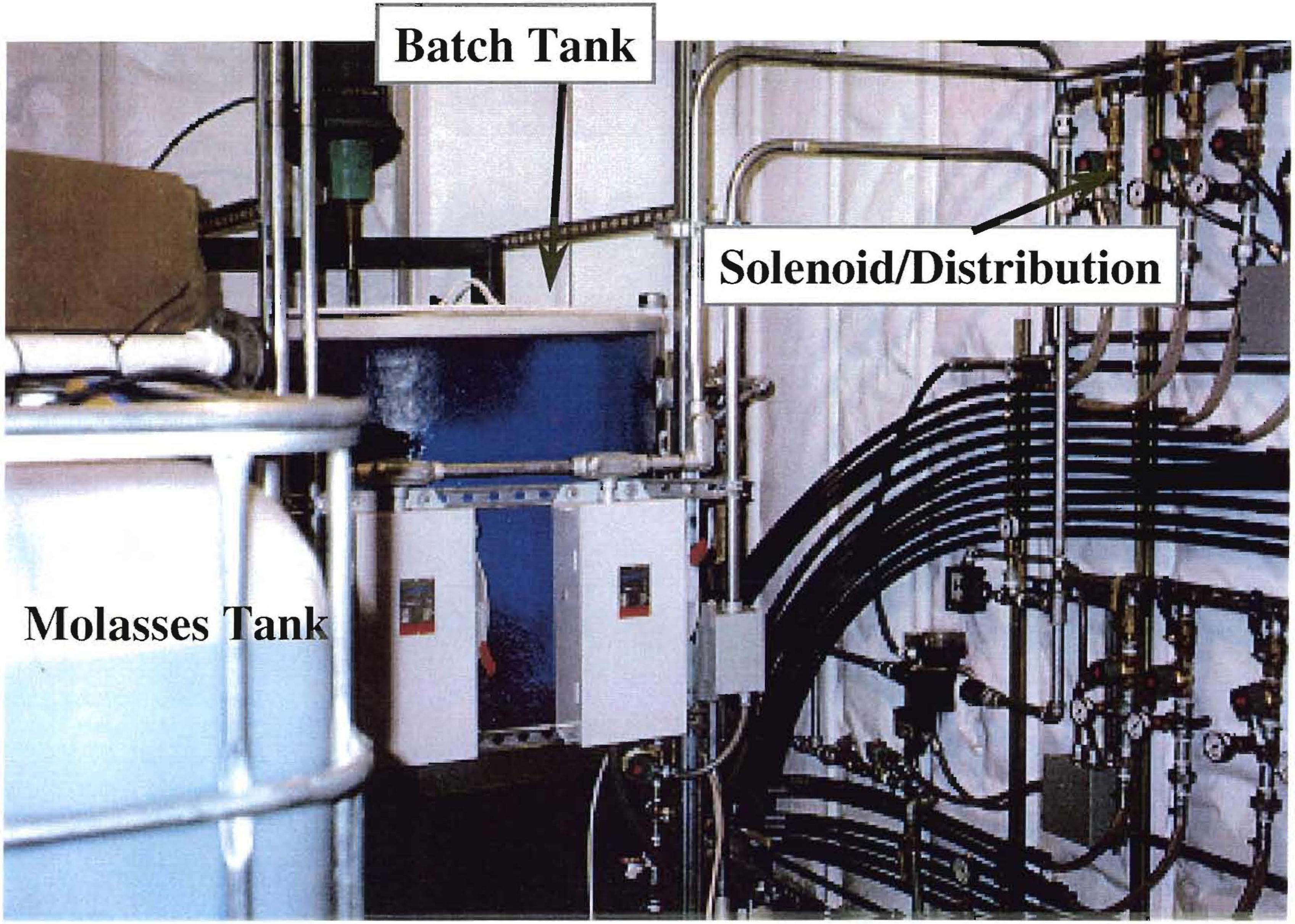


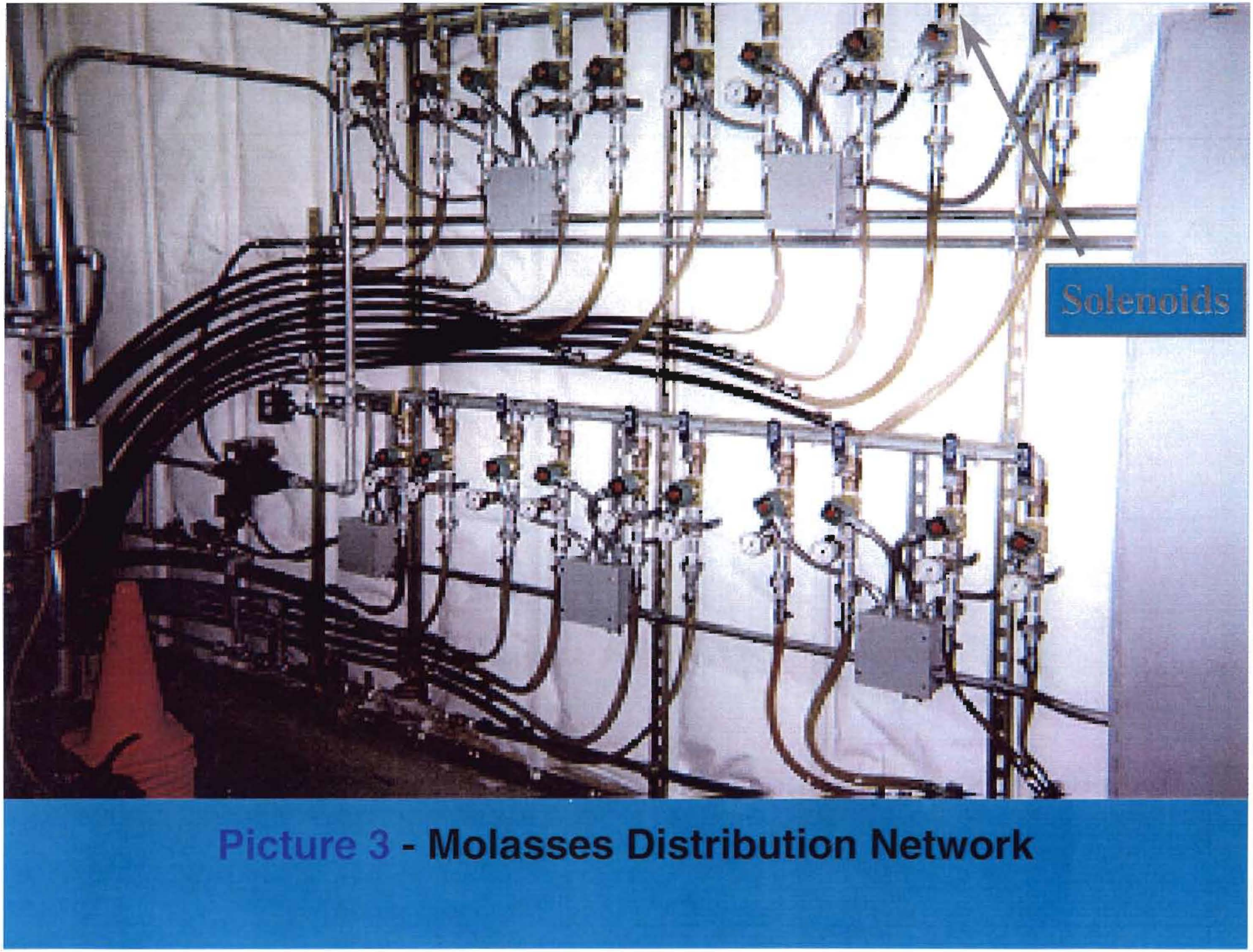
**Treatment Building**

Picture 1 Treatment Building



Picture 2 Molasses Injection System





Picture 3 - Molasses Distribution Network

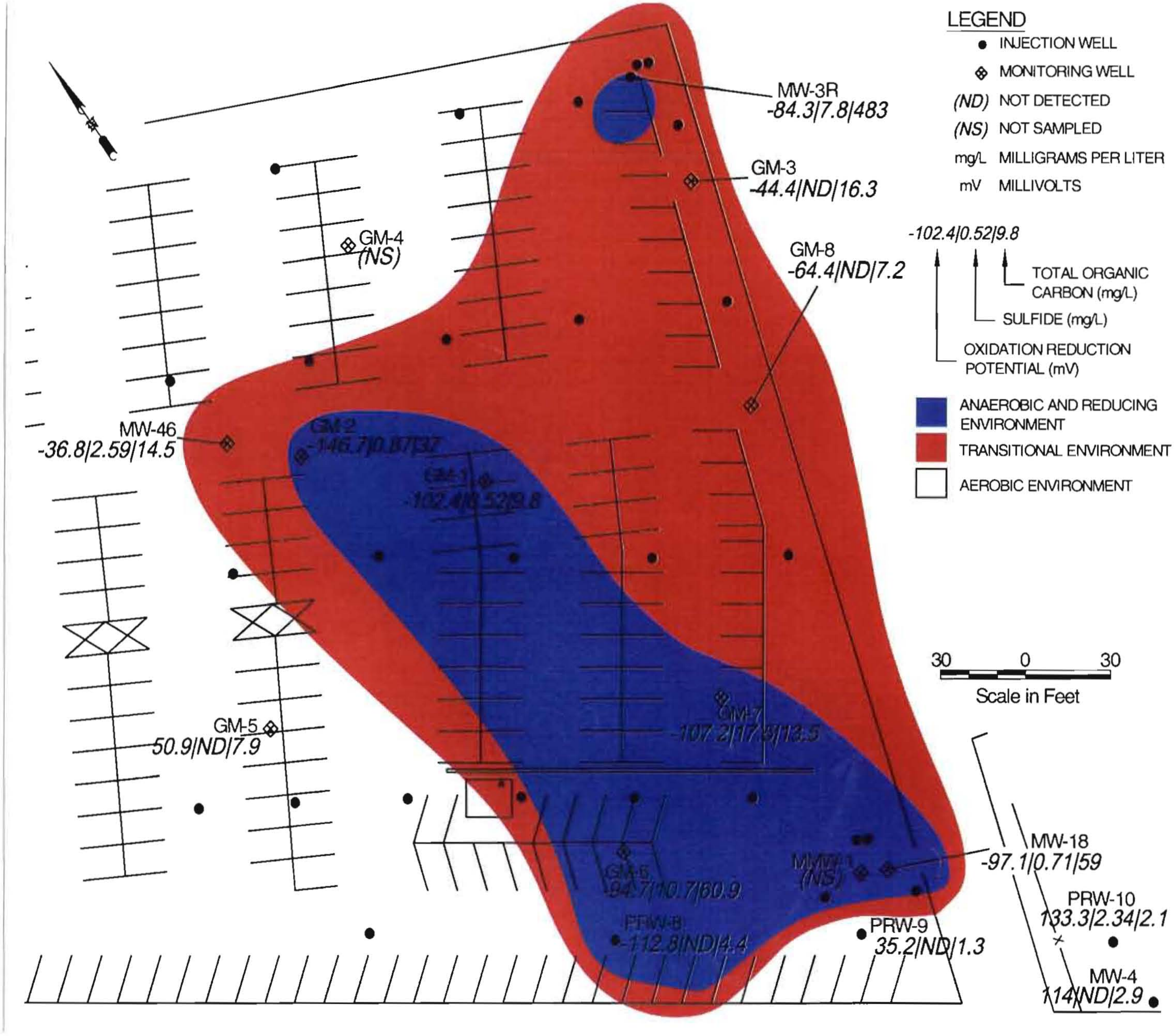


**Figure 5 - Distribution of Groundwater Indicator Parameters, Reactive Zone Established, July 1998.**

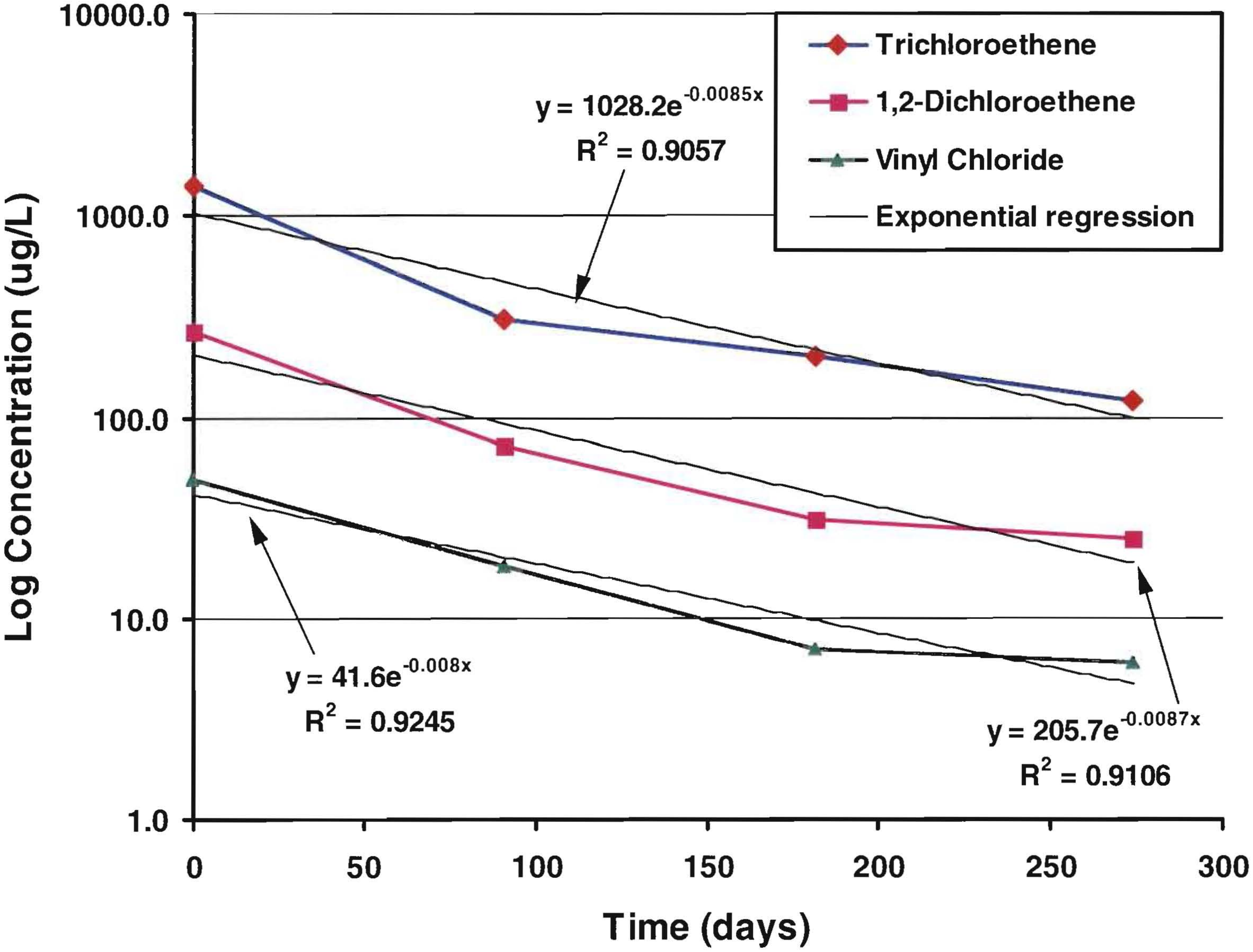


Figure 6 - Concentration Trends and Degradation Rates for COCs in Groundwater at Pilot Study Area

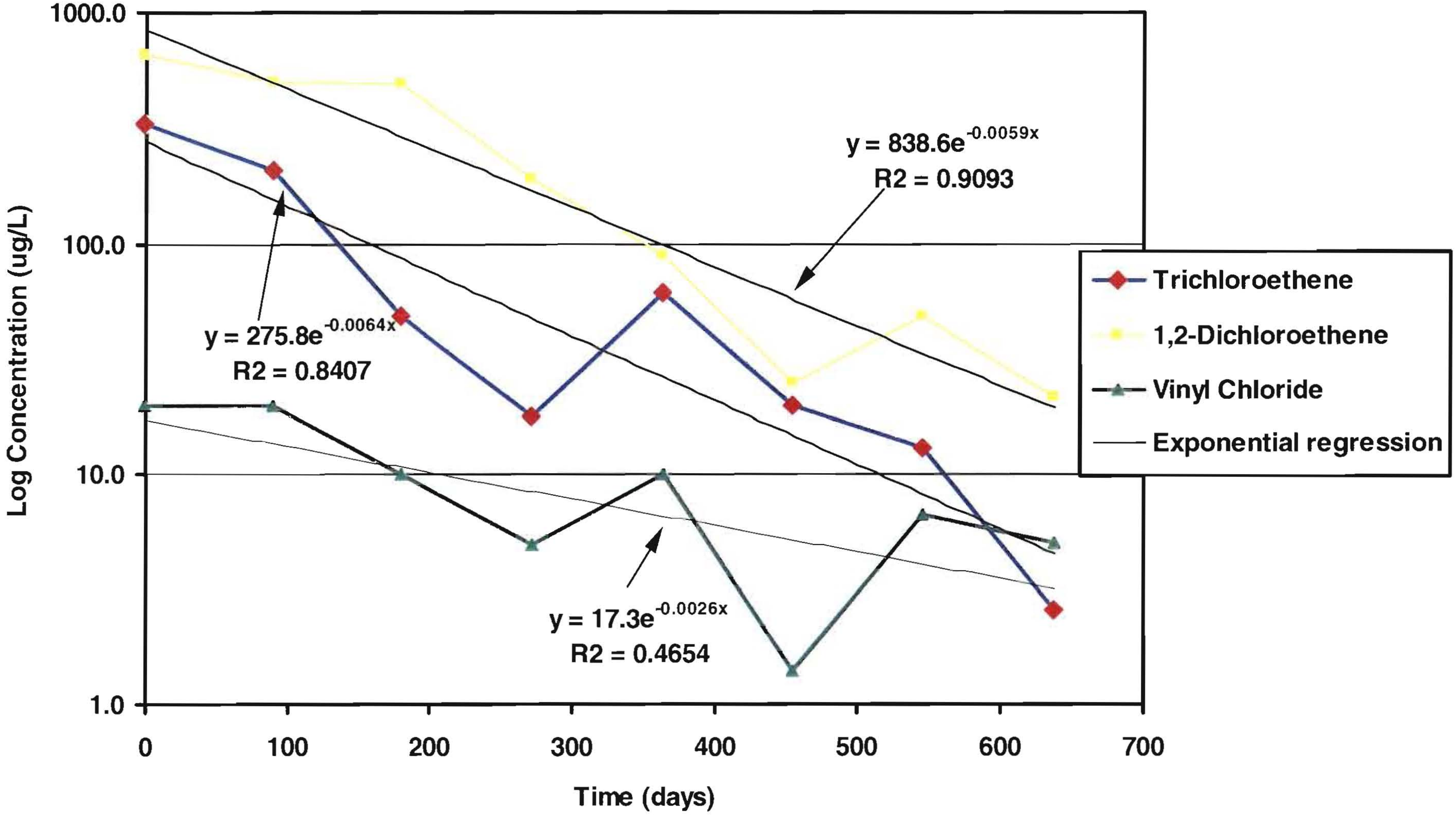


Figure 7 - Concentration Trends and Degradation Rates for COCs in Groundwater During Full Scale treatment

*Figure 8 $Cr^{6+}$ Plume January 1997*

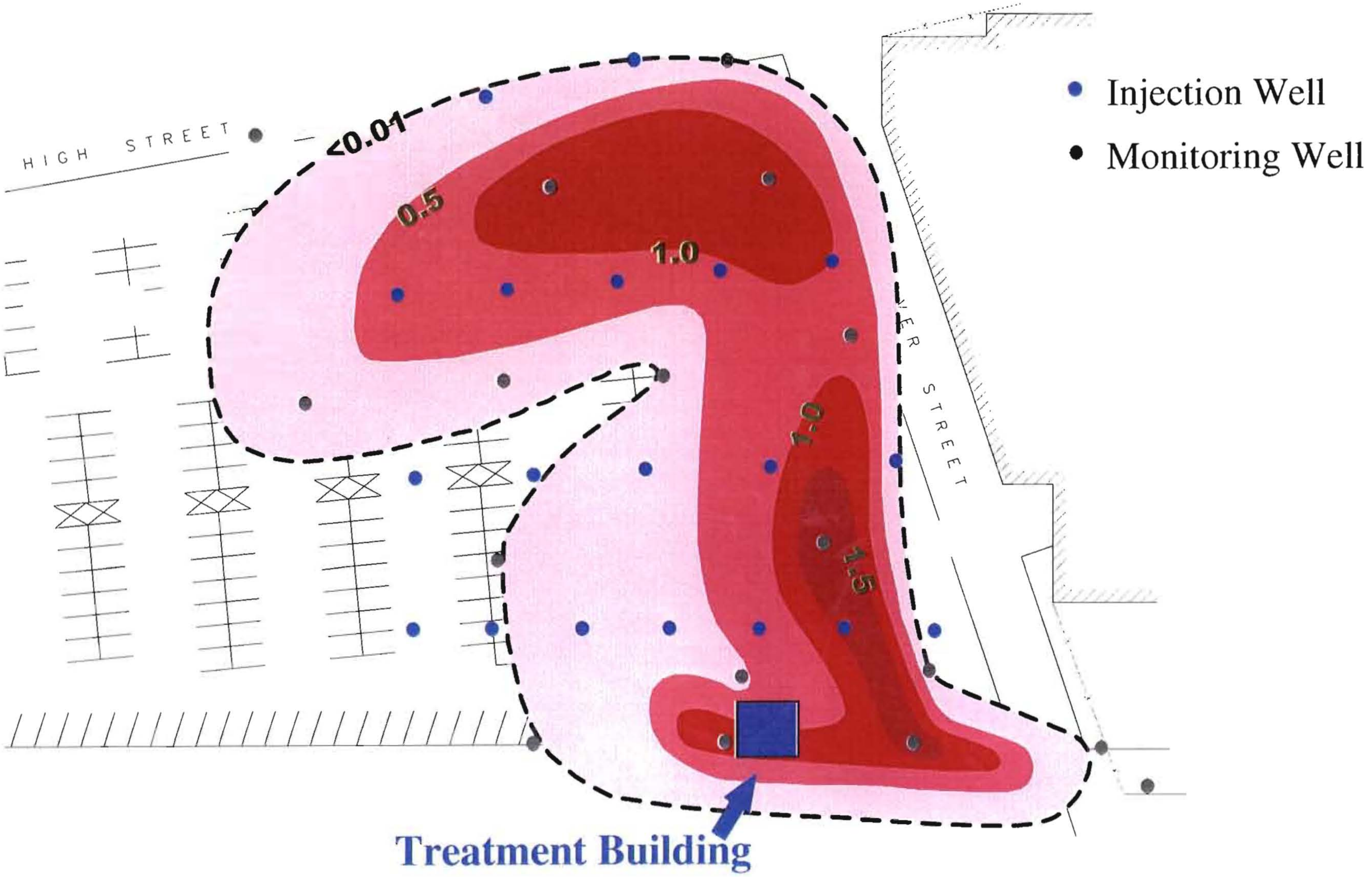
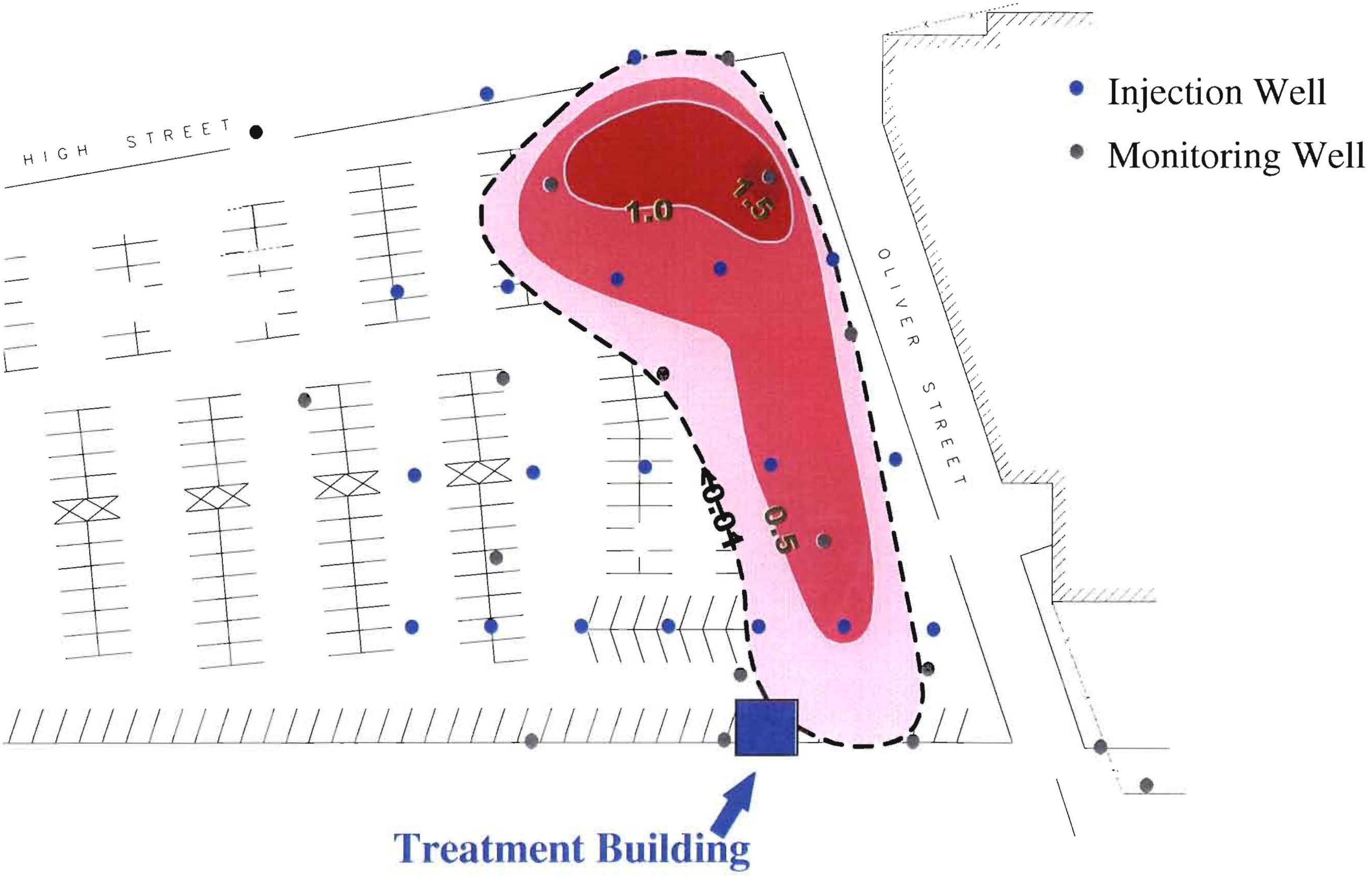
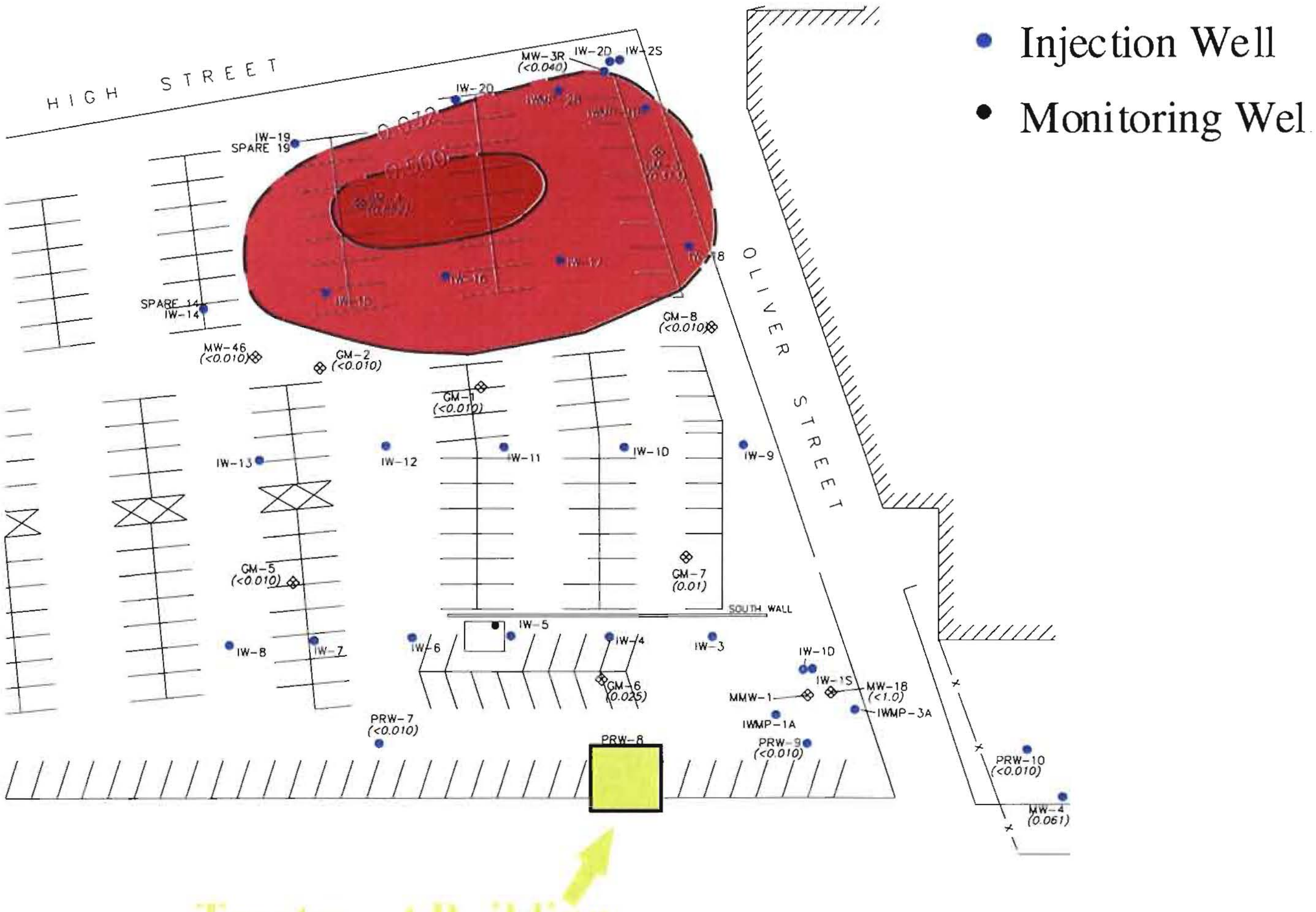


*Figure 9 $Cr^{6+}$ Plume November 1997*



## *Figure 10 Cr$^{6+}$ Plume July 1998*



- Injection Well
- Monitoring Wel

Treatment Building

# SITE 3

## Site 3 – ENHANCED REDUCTIVE DECHLORINATION OF PCE IN BEDROCK: Northeastern U.S.

Pilot and full-scale results are presented for the enhanced reductive dechlorination (ERD) of tetrachloroethene (PCE) in bedrock groundwater using an in-situ reactive zone (IRZ). The pilot test was implemented in the mid-portion of an approximately 3,000-foot long plume. Initial PCE groundwater concentrations were approximately 120 micrograms per liter (µg/L).

Historical groundwater monitoring data indicated volatile organic concentrations (VOC) concentrations were in equilibrium throughout the plume, with little evidence of the degradation of PCE. Baseline biogeochemical sampling was performed, and the results indicated the environment in each area was aerobic to transitional. A review of the electron acceptor and donor analytical data indicated the rate of attenuation was also limited due to a lack of organic carbon (electron donor/substrate).

A pilot test was initiated that consisted of an injection well and two downgradient monitoring wells. A reagent of molasses and water was injected on a weekly to monthly interval. The results of the pilot tests indicate anaerobic and reducing conditions were established and organic carbon concentrations increased downgradient of the injection wells. The increased amount of organic carbon coupled with the anaerobic and reducing conditions promoted the reductive dechlorination of PCE to lesser chlorinated compounds (TCE, DCE, VC, and ethene). The increased rate of attenuation decreased the ratio of PCE to daughter products, and reduced overall VOC mass within the pilot test areas. The results of the 15-month long pilot test were used to implement a full-scale in-situ treatment system for the site. The following sections discuss the IRZ process and present more detail on the implementation and results of both the pilot and full scale approach at this site.

### Background

A tetrachloroethene (PCE) spill was discovered in 1985 at a northeastern United States manufacturing plant. A subsequent groundwater investigation resulted in the installation of approximately 40 wells to delineate the PCE plume. All site wells were installed in bedrock, which is a succession of Triassic-aged siltstones and shales. The overburden at the site consists of relatively thin and dry glacial till.

PCE has been delineated horizontally and vertically at the site, and a dissolved PCE plume has been defined. Low concentrations of PCE (1 µg/L) extend approximately 3,000 feet (914 meters) downgradient of the spill area. Historical groundwater monitoring indicates that the plume is currently at equilibrium. This is most likely a result of the low solubility and adsorption of PCE onto the aquifer material in and downgradient of the source area, and to a lesser degree from natural attenuation of PCE in various portions of the site. The distribution of PCE within the plume prior to initiation of the pilot test (February 1999) is provided (see Figure 1 "Distribution of PCE (µg/L) in Bedrock Groundwater").

Hydraulic control has been established at the site through pumping. Low concentrations of PCE breakdown products (such as TCE and cis-1,2-DCE) were detected in the former source area during the ongoing groundwater monitoring at the site, indicating that natural reductive dechlorination of PCE was taking place prior to initiating the ERD pilot test. The observed reductive dechlorination in the source area was a result of favorable geochemical conditions: anaerobic and reducing conditions and the presence of organic carbon (electron donor) in groundwater. Less favorable conditions that exist outside the former source area (more aerobic and oxygenated groundwater and a lack of electron donor) do not promote continued degradation of the PCE plume.

Soil vapor extraction (SVE) had been employed in the former source area at the site, but the mass recovery was low and had reached asymptotic levels. Pumping of groundwater in the former source area and upgradient of the stream has been ongoing at the site since 1987. The pumping remedy has been effective in protecting the stream and containing further migration of PCE from the site. However, due to the inefficiency of pump and treat, and the elevated long-term costs associated with this technology, ARCADIS evaluated the site in order to determine if a more cost effective and efficient remedy could be implemented.

A pilot test was initiated in October 1998 to evaluate if the rate of reductive dechlorination downgradient of the source area could be enhanced via an anaerobic IRZ. The IRZ technology involves the injection of a carbon amendment into groundwater to promote anaerobic and reducing conditions and provide the electron donor (carbon) necessary for microbial degradation.

### Geology/Hydrogeology

The overburden at the site consists of a thin layer of glacially deposited sands, silts, and clays and is approximately 10 to 20 feet (3 to 6 meters) thick. The overburden contains little groundwater and therefore the majority of the site wells were installed in bedrock, which consists of Triassic-aged, low-permeability siltstones and shales. Results of several pumping tests completed at the site indicate that the bedrock at the site has a hydraulic conductivity (K) in the range of 0.14 to 1.78 feet per day (0.04 to 0.54 meter per day). The groundwater velocity for the site is within a range of approximately 10 to 70 feet per year (3.1 to 21.3 meters per year).

The bedrock is primarily fractured along horizontal bedding planes that strike to the northwest with a slight dip (9°) to the northeast. Minor vertical fractures are also present in the bedrock. Groundwater flow is believed to be primarily along the horizontal bedding plane partings that are coincident with the strike of the rock. Groundwater flow is generally south-southeast with the orientation of the plume being coincidental with strike. There is historical evidence supporting the interconnection of the bedding plane fractures through previous pumping and injection tests on the aquifer.

Monitoring and pumping wells have been installed in the bedrock to various depths ranging from 50 to 190 feet (15 to 58 meters) below land surface (bls).

### The ARCADIS Approach

The treatment approach employed at this site is the in-situ reactive zone (IRZ) technology. Reactive zones are simply treatment zones, developed in-situ, using selected reagents that enhance, or modify, subsurface conditions in order to fix or degrade target contaminants (see Figure2 "Reactive Zones"). These zones are typically created to intercept and treat mobile groundwater impacts, but are also being applied to less-mobile soil impacts. Ideally, reactive zones enhance natural conditions in order to speed up naturally occurring remedial processes (for example, enhancing an already reducing in-situ environment can accelerate the natural attenuation of chlorinated compounds).

In-situ reactive zones are applicable to a wide range of target contaminants. They have been applied, or are being tested on heavy metals (chromium, zinc, mercury, copper, lead and cadmium), chlorinated aliphatic hydrocarbons (CAHs) (trichloroethene, tetrachloroethene, 1,1,1-trichloroethane, carbon tetrachloride, and daughter products of these compounds), pentachlorophenol, and halogenated organic pesticides (1,2-dichloropropane [DCP] and 1,2-dibromo-3-chloropropane [DBCP]).

Reactive zones can take the form of a "reducing zone" or an "oxidizing zone". The choice is driven by two factors: the natural environment and the nature of the contaminant being targeted. In addition, reactive zones can be created by taking advantage of the activity of indigenous microbial populations (through the injection of degradable organic substrates, other electron donors, or electron acceptors) or through the addition of chemical reagents.

A this site, the IRZ is being applied as a microbially mediated reducing IRZ to target PCE impacted groundwater in a bedrock environment. Reducing reactive zones can be simply defined as artificially enhanced subsurface treatment zones, in which the environment is maintained as strongly reducing (i.e. the redox conditions are maintained well below 0.0 mV and dissolved oxygen below 1.0 mg/L). This environment can be maintained using the addition of naturally degradable organic mass. Degradable organic carbon – in the form of labile organic substrates such as sugars, lactate, etc. – is added to the subsurface. The indigenous heterotrophic microorganisms present in the aquifer readily degrade the organic carbon resulting in the utilization of available electron acceptors present in the groundwater. Starting with dissolved oxygen, the microbial population then uses nitrate, manganese, ferric iron, sulfate and finally carbon dioxide as electron acceptors. Depletion of these electron acceptors leads to successively more reducing conditions as the reduction-oxidation (redox) potential is lowered.

The favored approach is to use indigenous microbial populations. The bacterial population may be stressed due to the COC impacts, or the ability of the microbial population to degrade the COC mass may be limited by a lack of electron acceptors (dissolved oxygen, nitrates, manganese, iron, sulfates or carbon dioxide), or a lack of degradable organic carbon (electron donors). In order to take full advantage of the microbial population's ability to degrade organic mass, electron acceptors and electron donors can be added to the subsurface. In so doing, the microbial population is allowed to complete the remediation process in situ.

### COC Chemistry: Halogenated Aliphatic Hydrocarbons

One of the most common applications of the reactive zone technology is for the enhanced degradation of chlorinated aromatic hydrocarbons (CAHs) and other halogenated aliphatic hydrocarbons (HAHs). This is in part due to the widespread occurrence of CAHs in groundwater, but also as a result of the efficacy of the technology in handling CAHs. It was recognized in the middle to late 1980's that both aerobic and anaerobic bacterial populations naturally degraded petroleum hydrocarbons and BTEX, with aerobic populations providing the most rapid degradation rates. It wasn't until the early 1990's that the anaerobic degradation of CAHs was considered a viable mechanism in the remedial tool kit. Enhancing an anaerobic environment using reactive zones in order to accelerate the degradation of CAHs has only become an accepted practice in the last 2 to 3 years (refer to Nyer [1], Suthersan [2], Burdick [3], Cirpka [4] and Lenzo [5]).

The primary pathways for the CAHs are anaerobic pathways. For many of the more common COCs (such as TCE, 1,1,1-TCA, and PCE) the anaerobic pathways are particularly efficient due to the fact that these compounds are relatively oxidized and are thus susceptible to reductive dechlorination in a reducing environment. As the chlorine atoms are stripped from the parent CAH, and there are fewer chlorine atoms attached to the base alkene or alkane molecule, the resultant chlorinated aliphatic is more reduced - less oxidized - and thus less susceptible to reductive dechlorination. Conversely, the more reduced forms (less chlorinated) are more easily oxidized than reduced and thus can be degraded under more highly oxidized conditions. An excellent example of this is the degradation sequence for PCE (see Figure 3 "Reductive Dechlorination of Tetrachloroethylene"). PCE and TCE are readily reduced under anaerobic and reducing conditions, however it takes more and more aggressively reducing conditions to achieve the degradation of TCE to DCE and DCE to VC and finally vinyl chloride to ethene.

### Baseline Biogeochemical Assessment

A baseline biogeochemical sampling event was performed prior to initiating the pilot test to determine background conditions at the site, and to evaluate the biogeochemical environments present in various portions of the plume, including the pilot test area. Groundwater samples were collected utilizing low-flow sampling procedures from a background well located upgradient of the assumed source area and the pilot test area. Field parameters (dissolved oxygen (DO), oxidation-reduction potential [ORP], pH, temperature, and conductivity) were collected at the well head using a flow-through cell and a multi-meter, and samples were collected for a full suite of biogeochemical parameters. The laboratory parameters included VOCs, alkalinity, ammonia, biochemical oxygen demand, chemical oxygen demand, chloride, total and dissolved iron and manganese, nitrate/nitrite, sulfate/sulfide, dissolved organic carbon (DOC), and total organic carbon (TOC). Samples were also analyzed in the field utilizing a spectrophotometer for ferrous iron and sulfide, and submitted to a specialty lab for analysis of permanent gases (carbon dioxide, oxygen, nitrogen, methane, and carbon dioxide) and light hydrocarbons (methane, ethene and ethane).

The background biogeochemical environment flowing onto the site was aerobic (DO = 7.09 mg/L) and oxidizing (ORP +42.7millivolts [mV]). VOCs were not detected at this upgradient location. Background groundwater contained low levels of some electron acceptors: non detectable levels of nitrate; < 1 mg/L of iron and manganese; and carbon dioxide concentrations of 9.7 mg/L. Ethene and ethane, the final products of reductive dechlorination of PCE, were non detect (< 5 nanograms per liter [ng/L]) in upgradient groundwater.

The baseline biogeochemical environment in the pilot test area was transitional: DO levels indicated anaerobic conditions in two of the three pilot test wells, while ORP levels were in the +19 to +160 mV range. Total VOCs in this portion of the plume ranged from 1 to 813 µg/L. The only PCE degradation product detected was TCE in two of the three pilot test wells. Levels of ethene and ethane were low and not significantly above background, indicating that little natural reductive dechlorination was ongoing in this portion of the plume.

The pilot test wells showed a significant increase (compared to background) in the amount of nitrate in the groundwater during the baseline sampling event, which could also be a result of lawn watering (and fertilizer). Detectable concentrations of ammonia and the most elevated level of dissolved nitrogen detected during the initial baseline assessment at the site were also identified in this area, suggesting that some of the nitrate is being reduced in this area. ORP measurements suggest that the environment may be favorable for denitrification.

### ERD Pilot Study

Wells associated with the pilot test are shown in Figure 4 "Pilot Test Area". Reagent injections were initiated in October 1998. Approximately 200-gallons of reagent was initially injected under pressure on a weekly basis and consisted of a 10:1 strength (ratio of water to molasses). Molasses was used as the electron donor due to its relatively low cost ($0.30/lb), high organic carbon content (approximately 60% by weight), and its ability to create a strong reducing environment in a short time period (as opposed to some other electron donors and delivery techniques that rely on dissolution and diffusion). The frequency of injection was modified to bi-weekly in May 1999, and the strength of the reagent varied from a 10:1 to 20:1 ratio based on the process monitoring performed during the pilot test. The reagent was injected under pressure (up to 30 psi) for a more thorough and rapid distribution into the bedrock aquifer system. Parameters associated with the performance monitoring focused on PCE and associated degradation products, DO, ORP, TOC and ethene.

Process monitoring was initiated in December 1998, approximately two months after commencement of the pilot test to monitor the development of the IRZ. Process monitoring events focused on field parameters (primarily DO and ORP) and measuring TOC concentrations in groundwater. Performance monitoring for VOCs was initiated after a TOC gradient had been established within groundwater in the pilot test area.

During the December 1998 process monitoring event, anaerobic and reducing conditions had been established in the injection well and first downgradient monitoring well (MW-1). TOC concentrations had significantly increased in the injection well, but little change in TOC concentrations were observed in the two downgradient wells. Little change was observed in the farthest downgradient monitoring well (MW-2).

In January 1999, the injection well was deepened by 10 feet (3 meters) to encounter a more highly fractured bedrock zone, and increase the ability to deliver the reagent to the more impacted portion of the aquifer. VOC concentrations in MW-1 significantly increased (PCE = 400 µg/L, TCE = 40 µg/L, and cis-1,2-DCE = 22 µg/L). This increase was due to a biological surfactant effect resulting from the increased microbial activity of the expanding microbial community. Reductive dechlorination was reducing an increased amount of TCE to cis-1,2-DCE, but increased rates of the reductive dechlorination of PCE to TCE were not occurring. The ratio of PCE to TCE during the background sampling event was 9:1; this ratio was 10:1 in February 1999, presumably due to desorption of VOCs from the aquifer matrix due to the creation of natural surfactants. The ratio of PCE to TCE was 85:1 during the background sampling event, and this ratio was 18:1 during the initial surfactant effect. The increased degradation of TCE to DCE was due to the anaerobic and reducing conditions that had been established in the area of the well. However, significantly increased rates for the complete reductive dechlorination of PCE to ethene could not occur since the electron donor (carbon) injected in IW-1 had not reached this downgradient location.

TOC concentrations continued to increase and the more strongly anaerobic and reducing conditions necessary for increased attenuation rates via reductive dechlorination were established in Well MW-1 through March 1999. Anaerobic and reducing conditions were present in IW-1, MW-1, and MW-3 during the April 1999 monitoring event, and aerobic and oxidizing conditions continued in MW-2. MW-3 is located adjacent to MW-2, and has a deeper open borehole interval. Monitoring was initiated in MW-3 since anaerobic and reducing conditions had not been observed in MW-2.

Elevated TOC concentrations continued to be present in the injection well (> 3,000 mg/L), and increased TOC concentrations (469 mg/L) were observed in downgradient Well MW-1. PCE concentrations in Well MW-1 had been reduced from 400 μg/L to < 5 μg/L. The reduced concentration was due to increased reductive dechlorination due to the availability of electron donor, and the ratio of PCE to TCE and DCE has also improved. The ratio of PCE to TCE was 4:1, and the ratio of DCE to PCE was 1.4:1. The most significant evidence for the increased rate of reductive dechlorination was the ethene data. Baseline concentrations in Well MW-1 for ethene were 12 ng/L. Ethene was detected at 408 ng/L during the April 1999 sampling event. Anaerobic and reducing conditions were present in Well MW-3 and ethene concentrations were also higher than background conditions (92 ng/L).

Subsequent monitoring events performed between May 1999 and August 2000 have indicated that the anaerobic and reducing conditions present in Wells IW-1, MW-1, and MW-3 have been maintained, and TOC concentrations in Well MW-1 have continued to increase. PCE and associated degradation products have continued to decline in Well MW-1. These declines are due to reductive dechlorination since significant increases in the concentration of ethene have been observed throughout this same time period. Increased TOC concentrations have not been observed in MW-3. This appears due to the increased rates of microbial activity upgradient of these wells. However, PCE concentrations in Well MW-3 continue to decline after a slight biological surfactant effect was observed in May 1999, and ethene concentrations continue to be more elevated than background conditions. PCE, cis-1,2-DCE, and ethene concentrations for MW-1 and MW-3 are shown in Figure 5 "MW-1 Pilot Data" and Figure 6 "MW-3 Pilot Data".

### Bulk Attenuation Rates

The rate by which a dissolved constituent attenuates at a particular site can be estimated through first-order kinetics. It is important to note that the calculation of attenuation rates are only approximations of the complex processes that are occurring in nature. It should further be noted that the attenuation rates presented in this section consist of the effects of both destructive (biotic attenuation) and non-destructive (dilution) mechanisms. Based on the minimal volume of reagent delivered to the aquifer, and the increases in degradation daughter products that have been observed at the site, the lowering of PCE mass that has been observed is believed to be effected minimally by dilution.

PCE concentrations versus time from August 1999 to August 2000 are plotted as shown (see Figure 7 "Reactive Zone Bulk Attenuation Rates"). A trendline for the exponential regression of PCE is also presented. The equation describing the exponential regression is posted on the plot. This is the equation describing the exponential regression, where the first order attenuation constant (k) is –0.008 and x represents time in days. The correlation coefficient (R2) is also presented. Regressions with values of R2 at and above 0.8 are generally considered to be useful.

Based on an attenuation constant (k) of –0.008, the half-life for PCE is approximately 80 days. This is significant due to the stable nature of the plume prior to the pilot test (little degradation) and in light of published half-lives for PCE in groundwater that range from 1 to 2 years (6). The results of the pilot test demonstrate that the rate of reductive dechlorination in the bedrock aquifer was enhanced by the reagent injections associated with the reactive zone. The increased concentration of organic carbon quickly established the anaerobic and reducing conditions necessary for the complete degradation of PCE to ethene in the injection well. The anaerobic and reducing conditions migrated from the injection well to a well located approximately 240 feet downgradient (MW-3). After initial desorption of PCE (presumably from a biological surfactant effect) PCE concentrations in the downgradient wells have declined to concentrations significantly below the equilibrium conditions present prior to initiation of the pilot test. This is considered significant due to the elevated levels of ethene concurrently measured during the test.

The amount of time necessary to observe a significant reduction in overall source mass indicates some conditioning of the microbial population was necessary to enhance the natural degradation mechanisms. However, bioaugmentation was not necessary to provide the microbial populations to the bedrock groundwater environment, demonstrating that the microbial populations in bedrock at this site were ubiquitous.

### FULL-SCALE SYSTEM

A full-scale IRZ system was installed at the site during the first quarter of 2000 and injections were initiated in May 2000. The reactive zone technology is also currently being evaluated in the source area (PCE concentration > 10,000 µg/L). The success of the ERD program has allowed for the discontinuation of groundwater extraction from some site wells, and will allow groundwater extraction to eventually be phased out for the site. This will result in a significantly more cost-effective groundwater remedy for the treatment of chlorinated VOCs in bedrock groundwater at this site compared to traditional alternatives.

The full-scale system consists of eleven injections wells located perpendicular to groundwater flow in two parallel lines between the source area and the stream. The wells are placed 70 feet on center along each line. The parallel lines of wells are approximately 250 feet apart. The full-scale injection wells have been used to establish a reactive zone throughout the impacted groundwater thus cutting off the source of mass to the downgradient plume. Eventually the downgradient portion of the plume will naturally attenuate. The full-scale system is expected to operate between two and five years before injections are terminated.

### CLOSING

In-situ reactive zones are rapidly becoming commonplace and, in many instances, replacing conventional remedial approaches. These applications are having the result of shortening the total time that it takes to complete a remediation project. Reactive zones are being applied in more varied environments – bedrock geology, high and low permeability unconsolidated geologic conditions – to treat a wider spectrum of compounds – CAHs, HOPs, PAHs, perchlorates – and in multiple medias – groundwater, soil and sediments. This case study is one example of the successful application of an IRZ to degrade CAHs.

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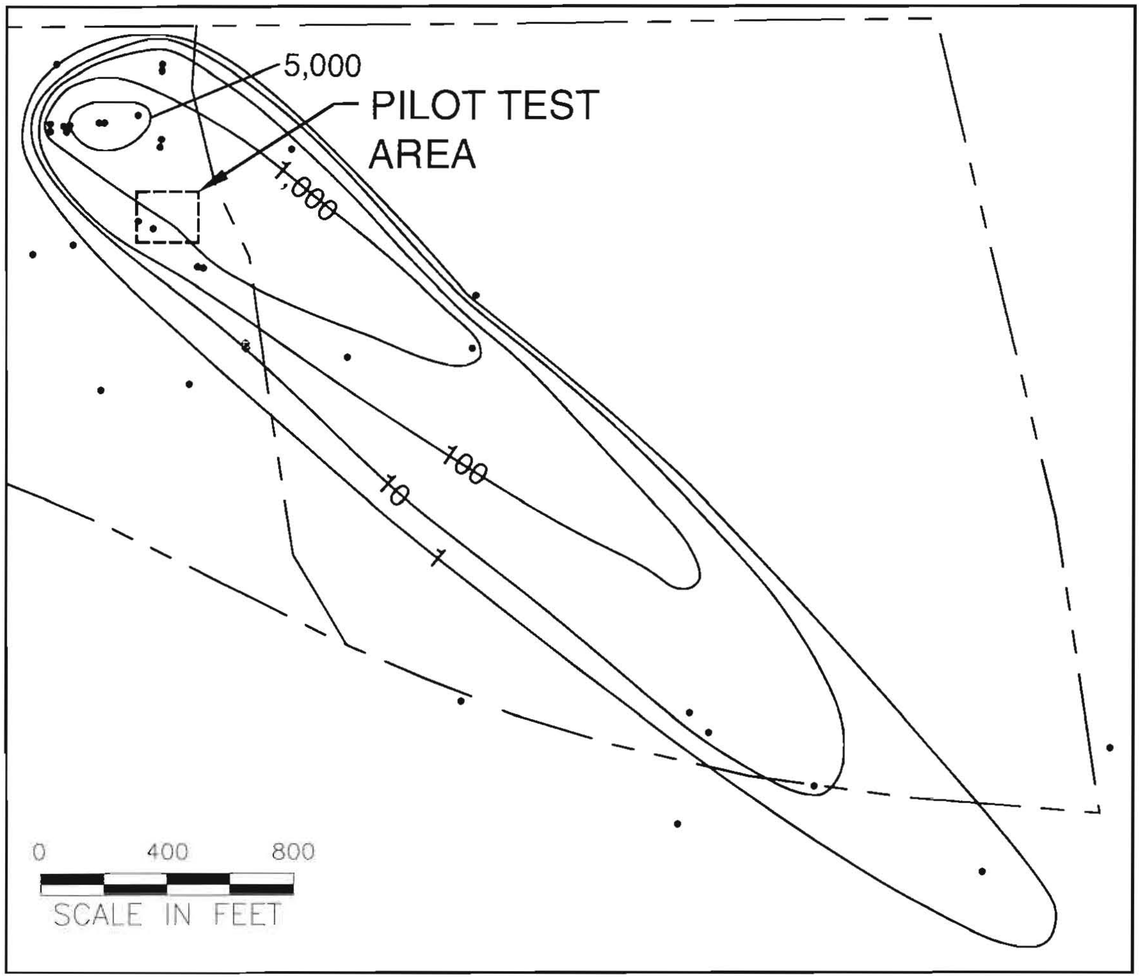
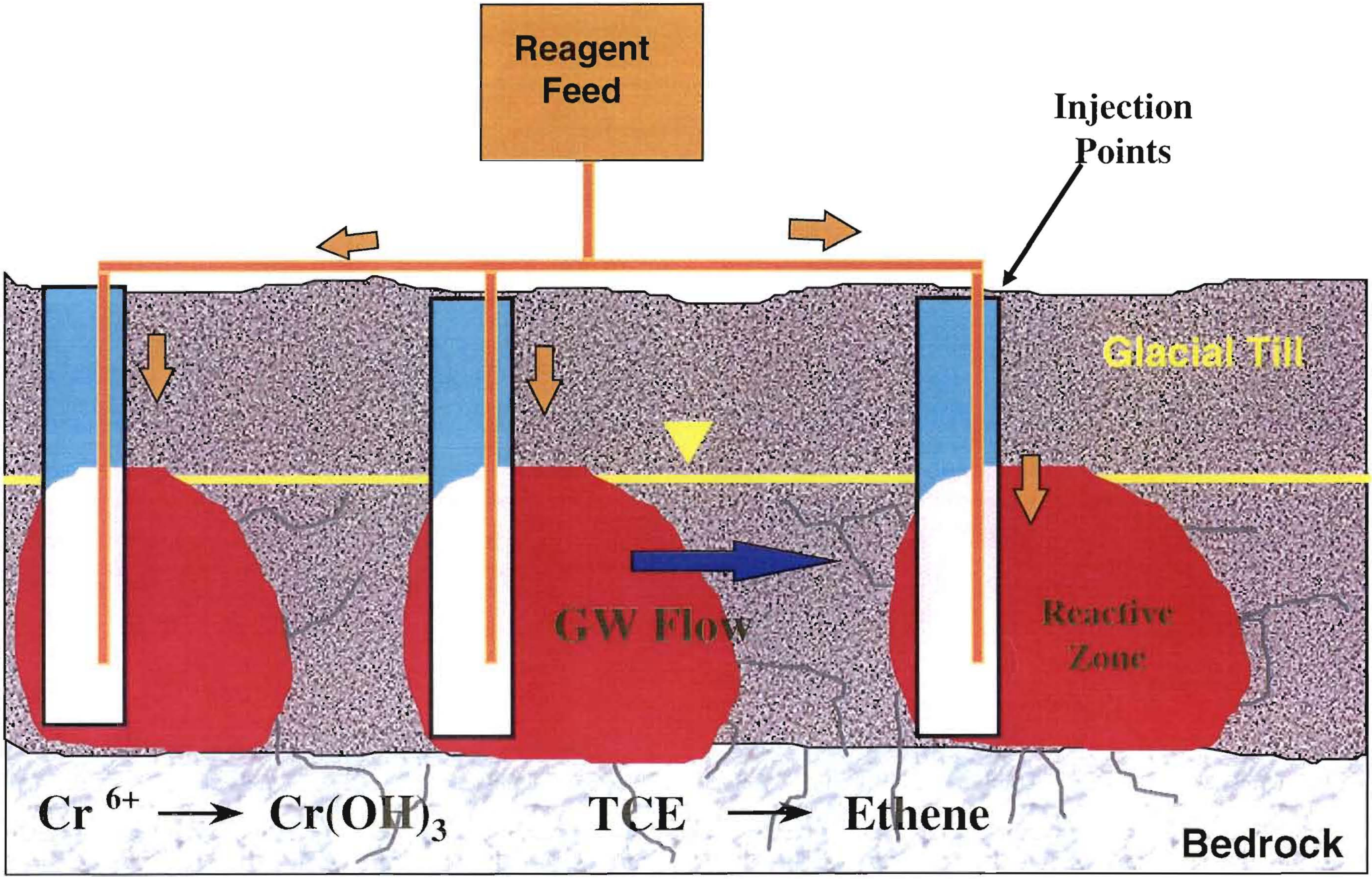
5. Lenzo, F.C. 1999. Remedial Technology Evolution – Science Meets Strategy in the Third Millennium. Strategic Environmental Management, vol. I, issue 3.

6. Howard, P., Boethling, R., et al. 1991. Handbook of Environmental Degradation Rates. Lewis, Boca Raton.

# Figure 1 - Distribution of PCE (μg/L) in Bedrock Groundwater

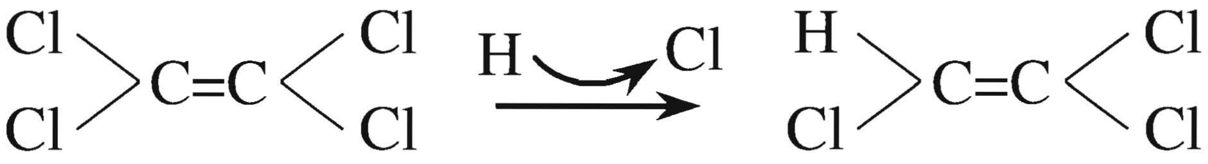


# Figure 2 - Reactive Zones



# Figure 3 - Reductive Dechlorination of Tetrachloroethylene

## PCE Degrades to TCE



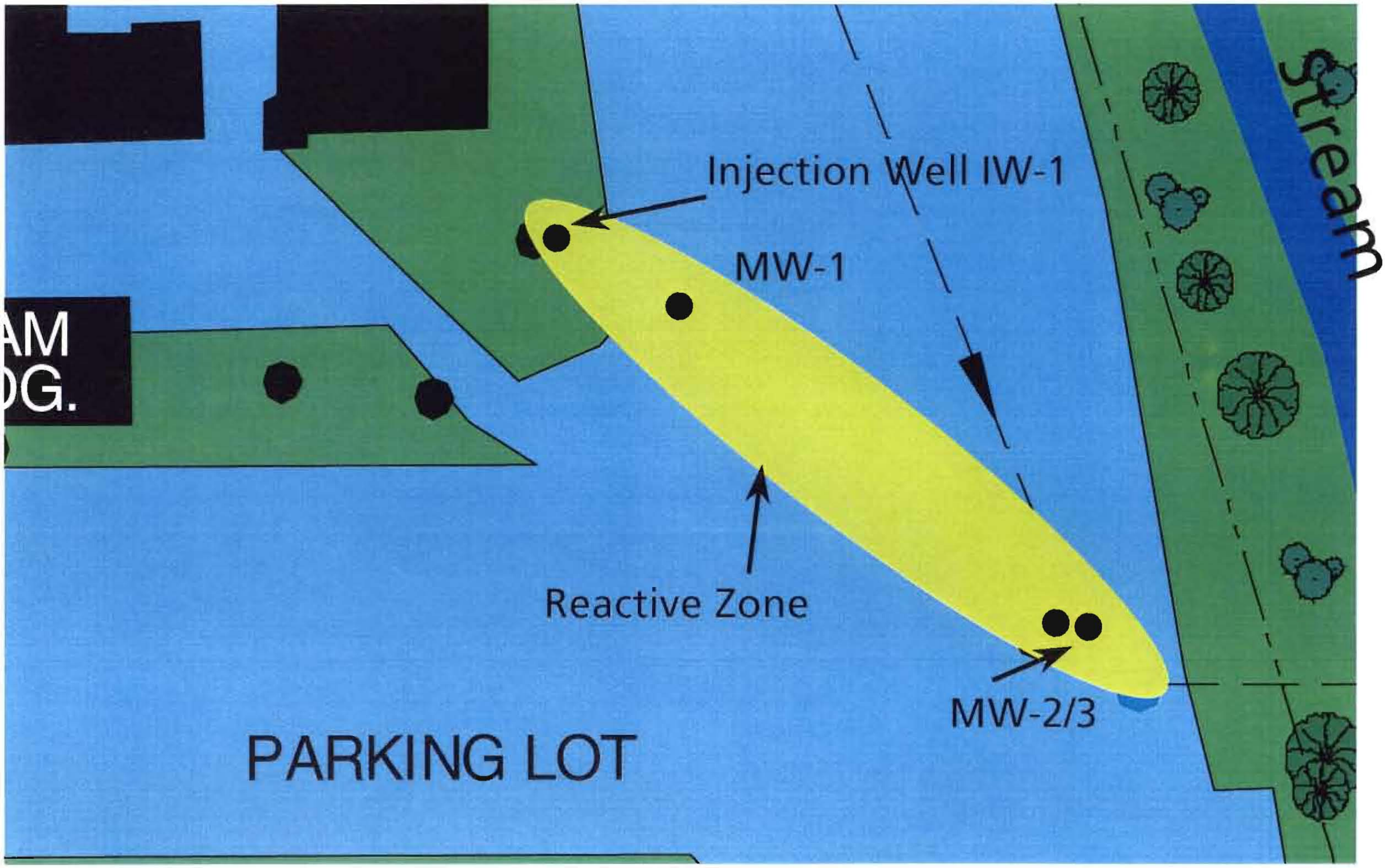
**PCE** **TCE**

## Full Degradation

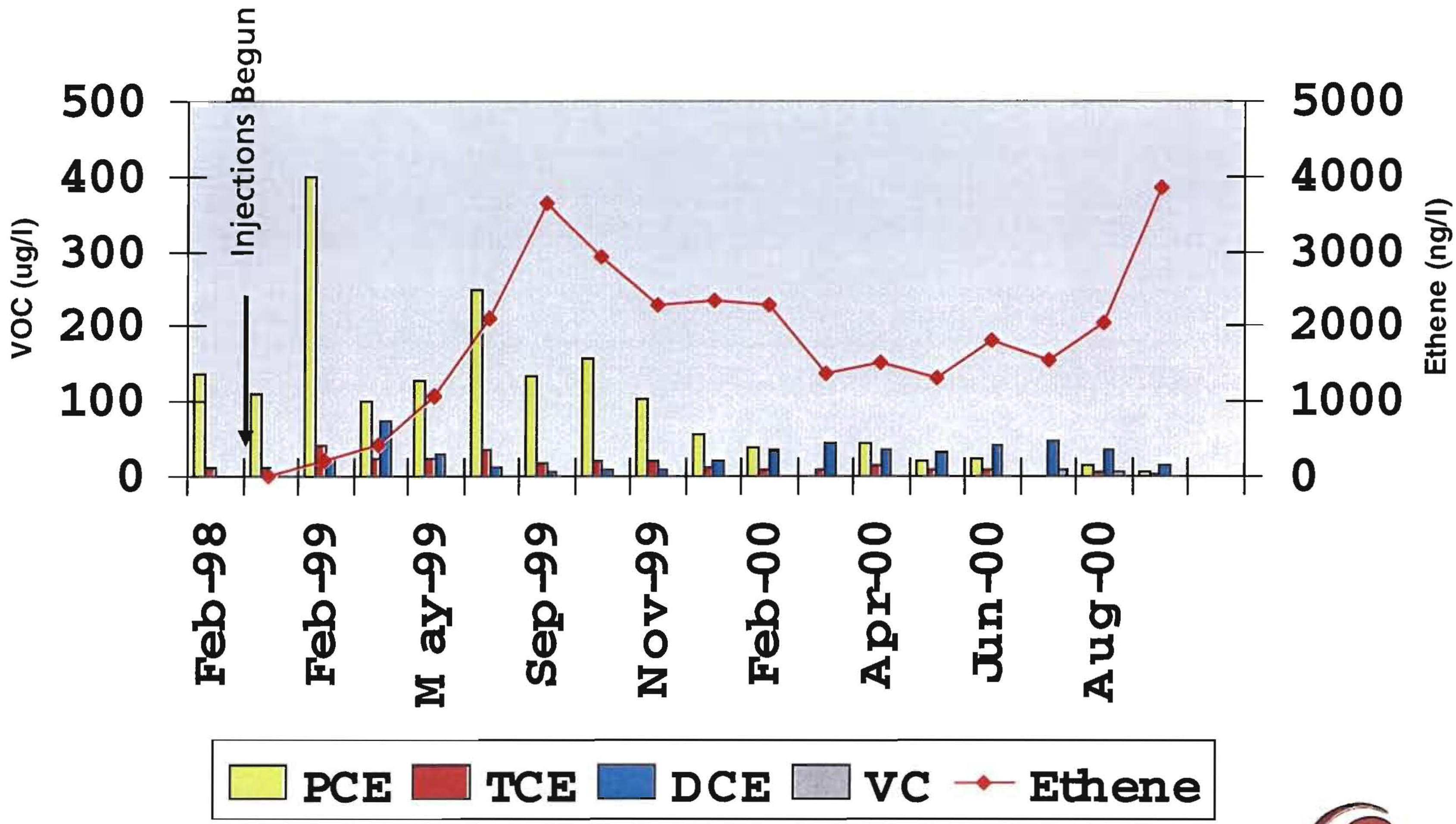
**PCE → TCE → DCE → VC → ETHENE → ETHANE → $CO_2$**

$CCl_2{=}CCl_2$ $CHCl{=}CCl_2$ $CHCl{=}CHCl$ $CH_2{=}CHCl$ $CH_2{=}CH_2$ $C_2H_6$ $CO_2$

Figure 4 - Pilot Test Area

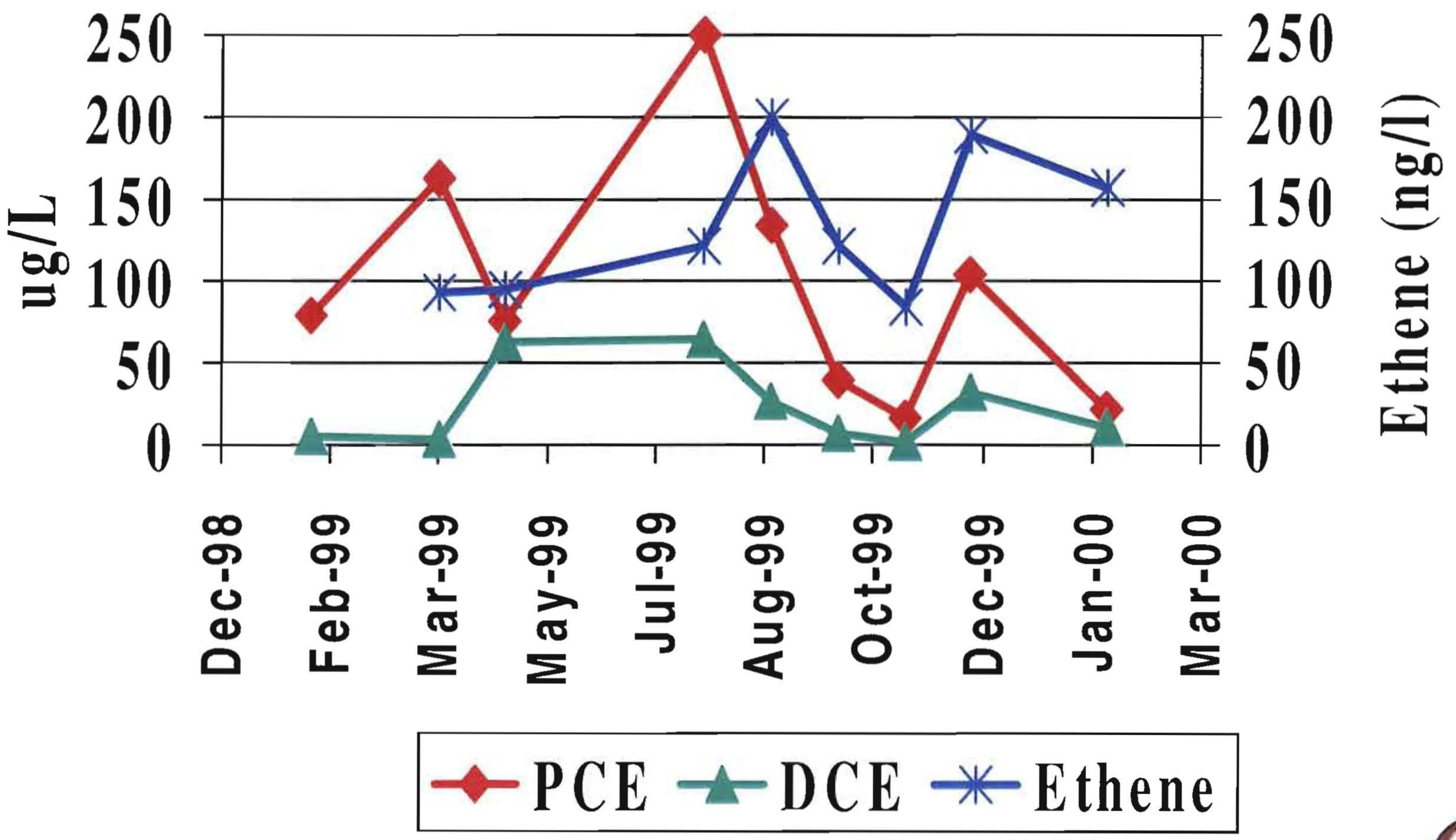


# Figure 5: MW-1 Pilot Data

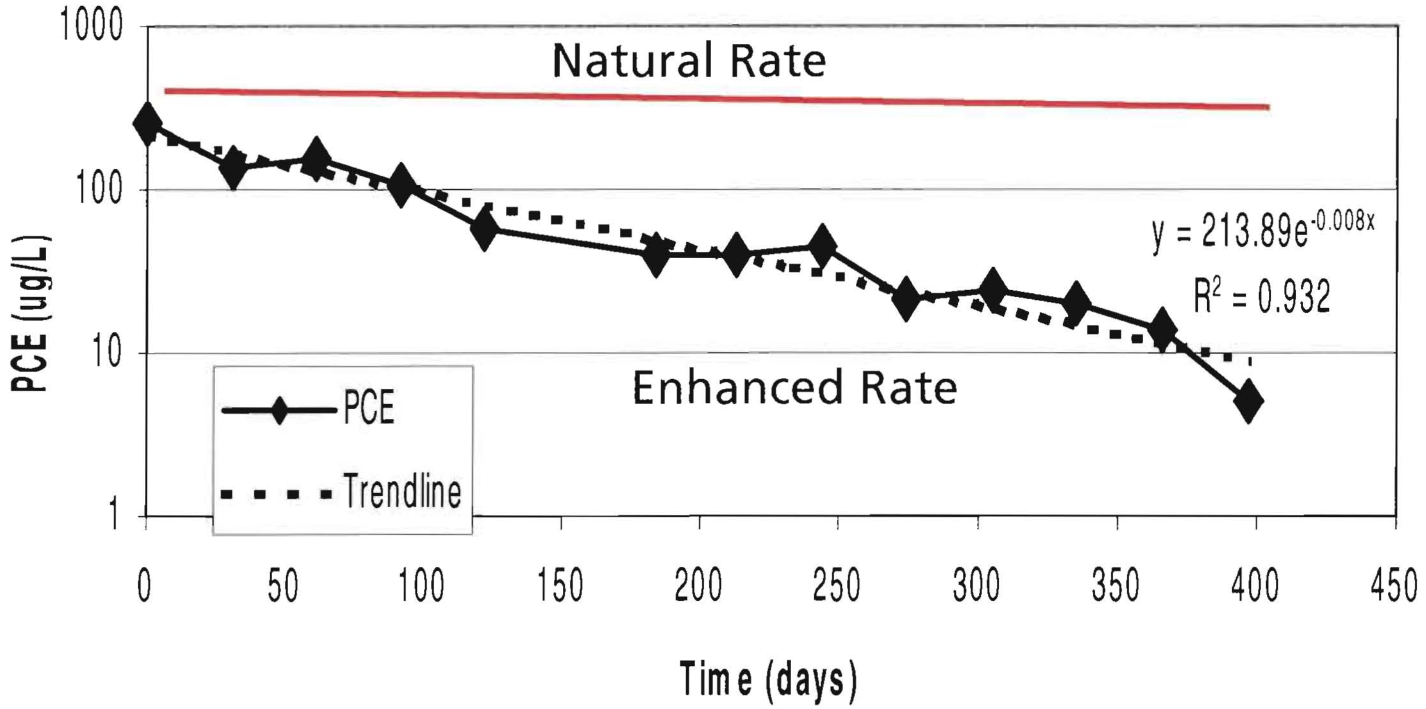


ARCADIS

# Figure 6 - MW-3 Pilot Data



# Figure 7: Reactive Zone Bulk Attenuation Rates



# SITE 4

### Site 4 – Manufacturing Facility, Southeast England

The results of a full-scale in-situ dechlorination treatment system are presented for a trichloroethene (TCE) groundwater plume located beneath an active manufacturing facility in Southeast England. The full-scale system was integrated into the construction of an expanded facility. Injection wells were installed below the facility prior to construction and a carbon reagent tank was installed on the roof to facilitate gravity-fed injections. A vapor membrane was installed below the building as well as a small vapor recovery system to recover potential methane, hydrogen sulfide and vinyl chloride (VC) vapors during the reductive dechlorination process.

An electron donor reagent consisting of varying strengths of molasses and water has been injected via the gravity feed system since 1999. Reductive dechlorination has been enhanced at the site and the TCE is being reductively dechlorinated to cis-1, 2-dichloroethene (DCE) and VC. VC is currently being generated at the site, but is being dechlorinated to ethene. Below the building, TCE concentrations have been reduced from a baseline maximum concentration of 22 mg/L to 0.014 mg/L. VC concentrations have increased from 0.3 mg/L to 4.5 mg/L, while ethene concentrations have increased from 0.002 mg/L to 1.5 mg/L.

Operation of the molasses injection system has established anaerobic and reducing conditions and promoted the complete reductive dechlorination of TCE to ethene. The increased rate of attenuation decreased the ratio of TCE to daughter products, and reduced overall VOC mass below the building expansion and in downgradient groundwater. First order degradation rates calculated from two years of operational data indicate an average post treatment half-life for TCE of 79 days and a half-life for cis DCE of 200 days.

### Background

In order to accommodate the manufacturing of a new product line, a building expansion was proposed for an area immediately adjacent to an existing manufacturing facility located in Southeast England. A historical trichloroethene (TCE) release in the older building had resulted in a VOC plume in groundwater emanating approximately 200-m downgradient of the historical building (Figure 1). Maximum TCE concentrations observed prior to treatment were approximately 22 mg/L. The plume is located in a sand and gravel aquifer, located approximately 6 meters below grade (Figure 2). The sand and gravel unit is very permeable, with a hydraulic conductivity that ranges between 0.01 and 0.001 m/sec. Given the gradient observed at the site (0.003), this equates to a groundwater velocity that ranges between 0.86 and 8.65 m/day

### The ARCADIS Approach

The footprint of the planned expansion building was located directly over 2/3 of the plume. Originally, an air sparging system was planned to be installed below the new building slab. However concerns were raised on the short-circuiting of airflow towards the more then 300 gravel-driven piles used to support the slab. Additionally, a significant vapor extraction, recovery and treatment system would have been required under this treatment strategy. Given these uncertainties, and the elevated costs associated with both capital and long term operation and maintenance of a large sparge/SVE system, alternative remediation strategies were explored. The strategy proposed by ARCADIS consisted of an in-situ reagent injection scheme that could be installed beneath the proposed building and then maintained with minimal disturbances to the future operational activities within the building. The strategy consisted of injecting an electron donor substrate to the groundwater in order to stimulate anaerobic reductive dechlorination of TCE (or enhanced reductive dechlorination [ERD]), while also maintaining a low negative pressure below the building to allow for venting of vapors to the roof. The injection system consisted of a mixing tank installed on the roof and automated controls to allow for the injection of a dilute molasses reagent on a daily basis. Baseline groundwater data was collected in 1997 to evaluate groundwater chemistry. The system and building were constructed in 1998 and the treatment system went on line in 1999.

Electron donor feed rates were initially low, so that the effects of vapor production and recovery could be evaluated and managed. Donor strength has been increased over the period of operation, and the plume has been reduced from maximum TCE concentrations of 22 mg/L to levels of TCE that are near the detection limit (0.001 mg/L). Accumulation of cis DCE and VC has been observed, however these concentrations are declining in most wells and mg/L levels of ethene have also been detected, indicating that the degradation has not stalled at the intermediates. The following sections describe the enhanced reductive dechlorination process, the design of the treatment system, operation and maintenance activities and also discuss and present the results from groundwater monitoring.

### Enhanced Reductive Dechlorination

Historically, chlorinated solvents have been considered relatively recalcitrant. As late as 1998, conventional remediation options for these sites were considered to be air stripping, granular activated carbon adsorption, and ultraviolet oxidation (Nyer 1998). Typically these technologies have been applied via pump-and-treat systems. These systems are well-known conventional technologies that are often associated with long term operations and prohibitively high maintenance costs. Because many contaminants possess a fairly low solubility and tend to partition preferentially to aquifer solids, pump-and-treat of groundwater is usually an ineffective means of mass removal. In-situ groundwater remediation approaches which can influence the partitioning effects of contaminants (or enhance desorption) will therefore offer distinct advantages, including significant reductions in the remedial lifespan, thereby lowering the cost of remediation.

Most chlorinated solvents will degrade or transform via reductive dechlorination. Reductive dechlorination describes the sequential replacement of chlorine atoms with hydrogen atoms. The chlorinated solvent may act as a primary electron acceptor via dehalorespiration, or be cometabolized under reducing conditions, including sulfate reduction and methanogenic environments (Vogel and McCarty 1985; Bradley and Chappelle, 1996). For reductive dechlorination to be thermodynamically favorable, the oxidation-reduction potential (ORP) must be sufficiently low, with neither dissolved oxygen (DO) nor nitrate available as terminal electron acceptors (Suthersan, 2002).

### In-Situ Reactive Zones.

*In-Situ* Reactive Zone (IRZ) technology is based on the concept of enhancing natural processes in a groundwater system to drive the conditions to a state that is more conducive to the degradation of a contaminant (in this case the chlorinated solvent) (Suthersan 1996, 2000). The IRZ application presented here involved the addition of a food grade solution of sugars and sulfur (molasses and water). A carbohydrate solution delivered to subsurface groundwater will act as an electron donor or supplemental energy source for microbes present in the subsurface and alter existing aerobic or mildly anoxic aquifers to highly anaerobic reactive zones, thus creating suitable conditions for the reductive dechlorination and treatment of the chlorinated solvent.

As discussed, one of the benefits of the IRZ technology is to influence the partitioning of the contaminants off of the aquifer solids (i.e. desorption), thereby making the dissolved mass more amenable to degradation or treatment. At a typical site, the amount of dissolved phase organic matter (present as contaminants) is only a small percentage of the organic matter present in the aquifer matrix. However, when an aquifer is flooded with excess dissolved organic carbon (uncontaminated matter) in the form of an IRZ delivering a carbohydrate, this partitioning equilibrium is upset. Simple equilibrium partitioning with the added carbon will drive a portion of the sorbed-phase contaminants into aqueous phase. This effect was observed by Hunchak-Kariouck, et al. (1997). Surfactants and co-solvents generated by the microbial population will also aid in desorbing contaminant mass (Payne 2000).

### Injection System Design

Prior to completion of the new building, two rows of injection wells were installed in trenches installed in the concrete slab of the new building floor (Figure 3). The northern and southern injection lines are oriented perpendicular to the orientation of the plume and groundwater flow. A total of 53 injection wells were installed (Figure 4). The treatment rows were designed to cut off the entire width of the plume, where it enters and exits the area beneath the building. Injection wells were installed to approximately six meters below ground surface, in a sand and gravel alluvium, which overlies the London Clay (a thick regional aquitard). Six vapor extraction wells were installed below the building in addition to a vapor membrane below the building (Figure 4). The injection lines were designed to be low profile so as not to disturb ongoing manufacturing activities (Picture 1). The trenches were covered with removable concrete vaults, to facilitate maintenance on the injection and SVE points.

Each injection well was connected to the automated reagent injection distribution system located on the roof of the building (Picture 2, Figure 5). The roof building contains a heated molasses holding tank, a mixing vessel, a potable water feed line, a small blower, a knockout tank, and the electrical controls for the system (Picture 3). The control panel allows for the selection of injection into individual injection points. This feature was important in the early stages of commissioning, when injections were gradually increased from 10 wells to 53 wells, while assessing vapor production. All injections are completed via gravity with an automated solenoid system, which delivers a pre-set volume and strength of reagent to individual wells.

Seven groundwater-monitoring wells were also installed at the site (Figure 3). Four of the monitoring wells were installed through the building foundation in order to assess groundwater chemistry and treatment effectiveness between the north and south injection lines (Wells 1, 2, 3, and 4). Three additional monitoring wells (Wells 5, 6 and 7) were installed downgradient and south of the southern injection line in the distal portion of the plume. A small scale LNAPL skimming system was also installed in the vicinity of Well 7. In this area the solvent plume co-mingles with dissolved phase petroleum hydrocarbons as well as LNAPL.

### System Start Up and Operation and Maintenance

The primary exposure pathway at the site is the potential for vapors to enter the manufacturing building above the plume. Groundwater in the shallow alluvium is not used for potable purposes, and sheet piling on the nearby river restricts groundwater discharge into the river. Given the scrutiny of the vapor exposure pathway, air modeling and a risk assessment was completed prior to system commissioning. This work identified action levels for vapors escaping to the building.

The system was commissioned gradually by slowly increasing the number of injection wells utilized and the strengths of the delivered reagent. Vapor monitoring was completed during this sale up period. The system was commissioned in June 1999, by injecting a 50:1 strength reagent into 10 injection wells along the northern injection line. Currently half of the injection points in each line are utilized. The system operates on a 24-hour cycle with injections occurring daily between 10 a.m. and 6 p.m. During the first two years of operation (June 1999 to June 2001), approximately 8,500 liters of raw molasses was delivered to the impacted groundwater at Enfield. This equates to a total of approximately 15,000 pounds of delivered organic carbon, or about 21 lbs. delivered per day to the entire plume. An increase in feed strength was initiated in September 2001 and is designed to foster more strongly reducing conditions to increase the mass removal rate of cis DCE and VC. The increased reagent strength results in an organic carbon dose of approximately 57 lbs./day. It should be noted that molasses was selected as the electron donor at this site due to its cost. The price for organic carbon in the form of molasses is only $0.2 per pound; making reagent costs a relatively small portion of the operation and maintenance (O&M) fees.

Current O&M consists of a molasses delivery about once per month (1,000 liters). Molasses is pumped from a delivery truck into a piping vault installed on the side of the building up into the holding tank in the treatment building. The temperature of the molasses is checked during the winter and summer to ensure that the viscosity of the molasses is low enough to allow for mixing, and not hot enough to promote extreme fermentation prior to injection. The tankage in the treatment building is also checked for biofilms, which are removed as necessary (approximately quarterly).

The most significant form of O&M has been related to the valves on the injection points. The system was shut down for 3 weeks in the first year of operation and a month in the second year due to degradation of the rubber seals in each solenoid valve at each of the injection points. These valves have since been replaced with Viton$^{TM}$ seals, which has corrected the problem. Quarterly groundwater monitoring is also part of the O&M.

### Results and Discussion

Low-flow (micro purge) groundwater sampling methods are used at the site to collect VOCs and sensitive biogeochemical parameters. All laboratory analysis is conducted locally in England. Baseline sampling was performed in October 1997. The baseline analysis indicated that anaerobic and reducing conditions were present downgradient of the building expansion and transitional conditions were present below the building expansion. The anaerobic and reducing conditions were attributed to the co-mingling of the chlorinated VOC plume with a plume of dissolved petroleum hydrocarbons. The presence of TCE degradation products (cis DCE, VC, and ethene) indicated that some microbial degradation was occurring in the natural environment. However, the biogeochemical environment observed below the building expansion was transitional (nitrate to iron reducing) and not strongly reducing enough to enable the complete dechlorination of the target VOCs (Table 1a, 1b).

**TABLE 1a. Summary of biogeochemical data (baseline; min/max).**

| | DO | ORP | PH | NITRATE | SULFATE | SULFIDE | IRON 2 | CHLORIDE |
|---|---|---|---|---|---|---|---|---|
| | (mg/l) | (mV) | (s.u.) | (mg/l) | (mg/l) | (mg/l) | (mg/l) | (mg/l) |
| Within | 3.68 | 37 | 6.63 | 0.6 | 160 | 2.4 | <0.10 | 59.5 |
| Plume | 4.80 | 76 | 6.81 | 0.7 | 210 | 3.0 | .9.0 | 80 |
| Distal | 3.7 | -66 | 7.1 | 0.2 | 190 | 2.2 | <0.10 | 58.5 |
| Plume | 4.9 | -123 | 7.8 | 0.6 | 210 | 2.4 | .4.0 | 67 |

**TABLE 1a. Summary of CVOCs, TOC and Degradation Products (baseline;min/max).**

| | TCE | C-DCE | VC | ETHENE | ETHANE | TOC | $CO_2$ | METHANE |
|---|---|---|---|---|---|---|---|---|
| | (mg/l) | (mg/L) | (mg/L) | (mg/l) | (mg/l) | (mg/l) | (mg/l) | (mg/l) |
| Within | 1.9 | 2.8 | 0.06 | <0.001 | 0.007 | 8.6 | 8.9 | 0.078 |
| Plume | 22 | 12 | 0.45 | 0.002 | 0.01 | 14.5 | 10.5 | 0.143 |
| Distal | 7.7 | 6.4 | 0.13 | <0.001 | 0.003 | 13.9 | 1.4 | 0.035 |
| Plume | 12 | 12 | 0.3. | 0.002 | 0.006 | 14.4 | 14.3 | 0.068 |

Twelve rounds of monitoring have been completed at the site since the system was initiated. Tables 2a and 2b summarize the ranges of various indicator parameters and VOCs that are present in the groundwater after two years of operation. It should be noted that even though 15,000 lbs. of organic carbon were delivered to the groundwater environment during this period, individual TOC measurements at monitoring wells located between and downgradient of the injection points have remained similar to baseline measurements. This is significant since TCE has been reduced from approximately 20 mg/L to 0.014 mg/L, without the relatively large carbon dosing employed at most IRZ sites. The accumulation of cis DCE and VC is being observed, however ethene detected in the mg/L range show that the solvents are being degraded to completion

**TABLE 2a. Summary of Post Treatment biogeochemical data (min/max).**

| | DO | ORP | PH | NITRATE | SULFATE | SULFIDE | IRON | CHLORIDE |
|---|---|---|---|---|---|---|---|---|
| | (mg/l) | (mV) | (s.u.) | (mg/l) | (mg/l) | (mg/l) | (mg/l) | (mg/l) |
| Within | 0.02 | -113- | 6.95 | Nd (<0.3) | 33 | 0.03 | 5.327 | 74 |
| Plume | 0.32 | 178 | 7.1 | 0.9 | 124 | 0.04 | | 157 |
| Distal | 0.01 | -62 | 6.95 | 0.7 | 38 | 0.03 | 0.594. | 79 |
| Plume | 0.26 | -98 | 7.15 | 3.5 | 107 | 0.04 | 2 | 102 |

**TABLE 2b. Summary of CVOCs, TOC and Degradation Products (post treatment;min/max).**

| | TCE | C-DCE | VC | ETHENE | ETHANE | TOC | $CO_2$ | METHANE |
|---|---|---|---|---|---|---|---|---|
| | (mg/l) | (mg/l) | (mg/l) | (mg/l) | (mg/l) | (mg/l) | (mg/l) | (mg/l) |
| Within<br>Plume | 0.003<br>0.014 | 0.056<br>20.8 | 0.009<br>4.5 | <0.001<br>1.1 | 0.008<br>0.08 | 8<br>11 | 915<br>1,188 | 0.03<br>3.3 |
| Distal<br>Plume | 0.002<br>0.003 | 0.164<br>0.370 | 0.303<br>0.514 | 0.31<br>0.78 | 0.037<br>0.17 | 8<br>9 | 2,735<br>3,280 | 3.4<br>4.2 |

Dissolved oxygen levels were significantly reduced throughout the entire treatment area footprint. Increases in iron, and decreases in nitrates and sulfates also indicate that a reducing environment was created at the site. Groundwater pH remained relatively neutral throughout the treatment process, indicating that the aquifer system contained sufficient buffering capacity. The TOC loading was low enough to avoid extreme fermentation and by-product formation.

## Summary and Conclusions

Operation of the molasses injection system has established anaerobic and reducing conditions and promoted the complete reductive dechlorination of TCE to ethene at the England Site. The increased rate of attenuation decreased the ratio of TCE to daughter products, and reduced overall VOC mass below the building expansion. First order degradation rates calculated from two years of operational data indicate an average post treatment half life for TCE of 79 days and a half life for cis DCE of 200 days (see Figure 6). Half lives as low as 14 days have been observed for TCE at other ARCADIS IRZ sites, however given the caution employed here in dosing due to vapor concerns, the England rates are acceptable . The plume has not moved outside of the treatment area and an increase in TOC dosing is expected to help increase the rates of treatment for DCE and VC in the future.

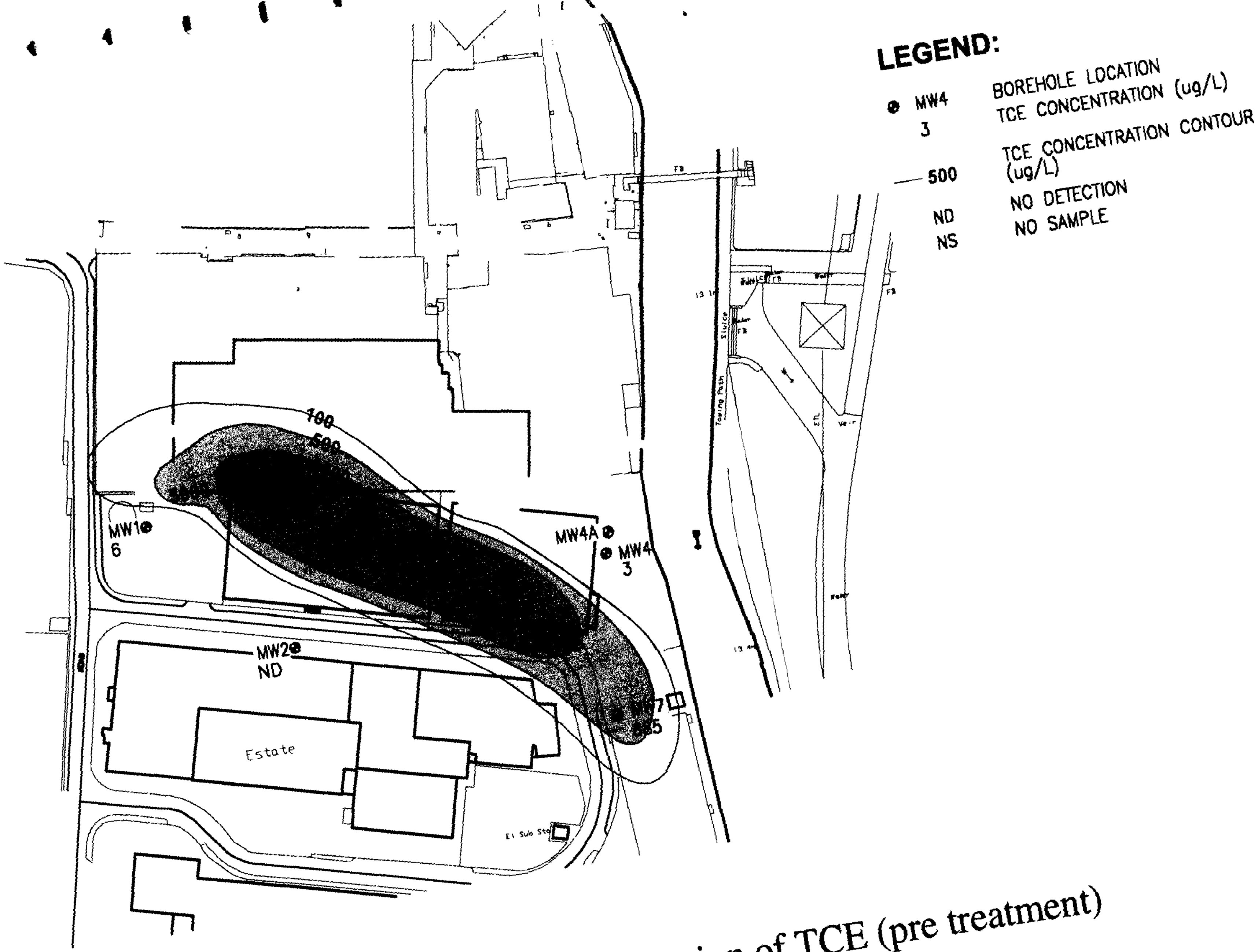
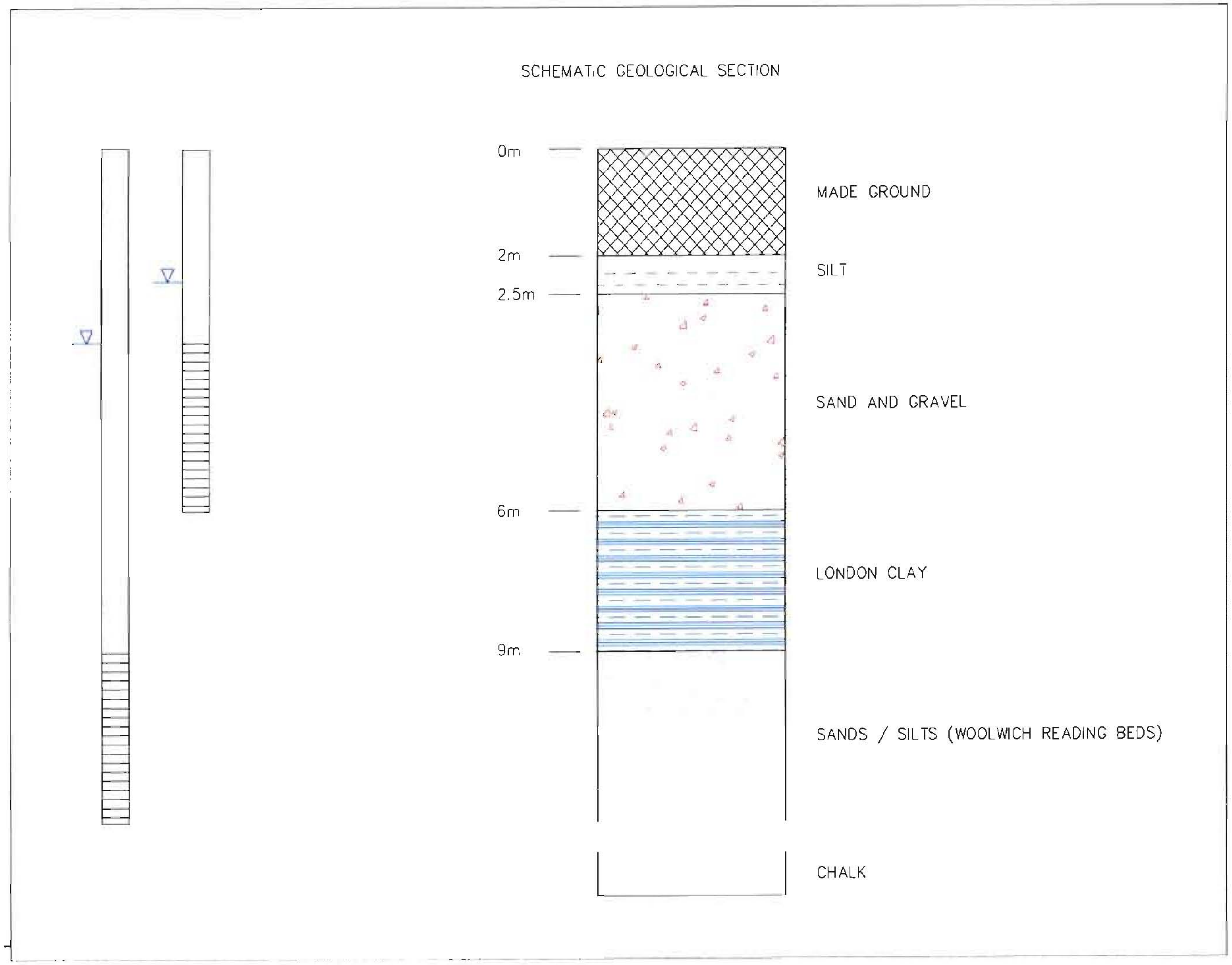


Figure 1: Distribution of TCE (pre treatment)

# Figure 2 Site Hydrogeology



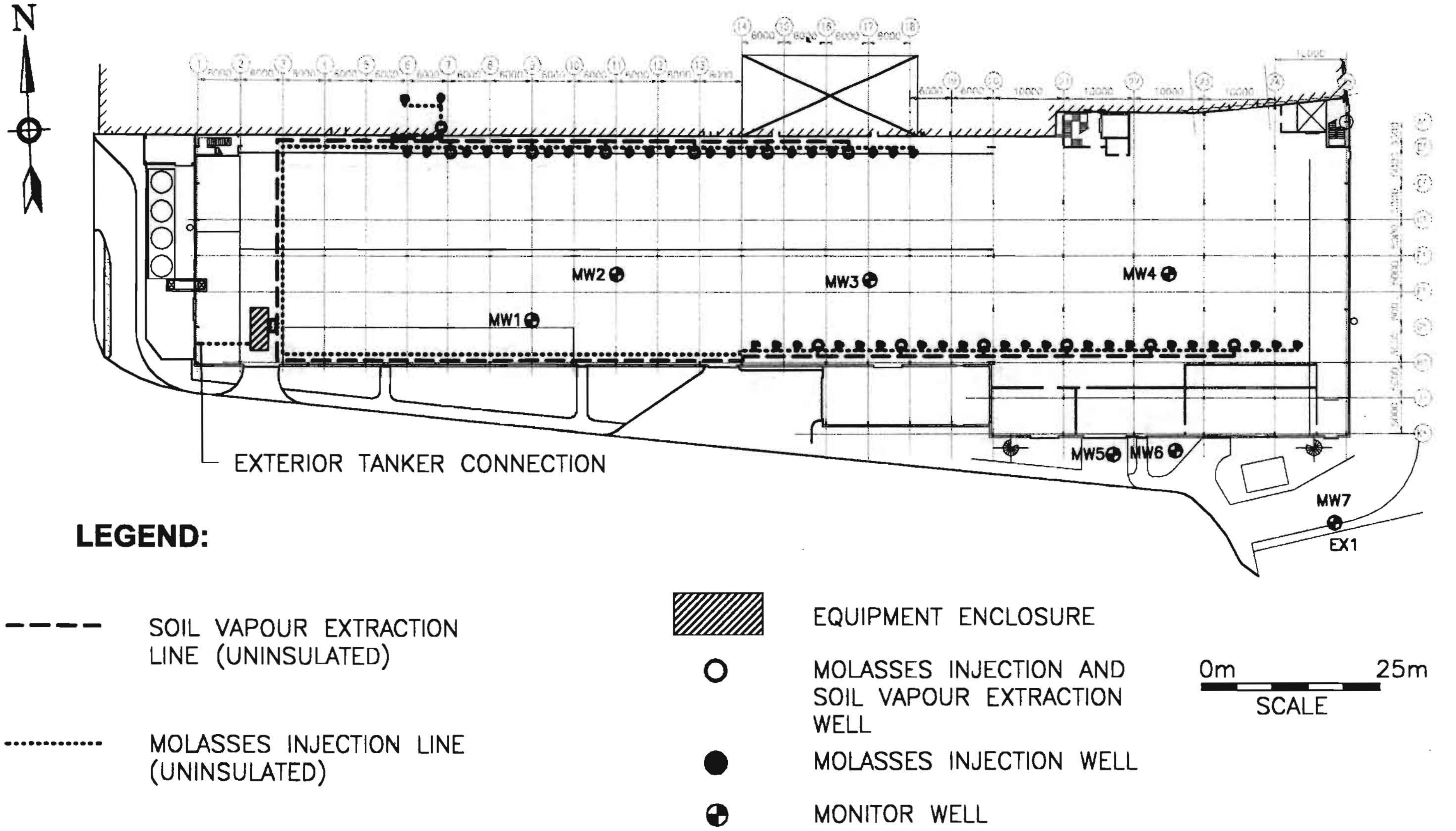
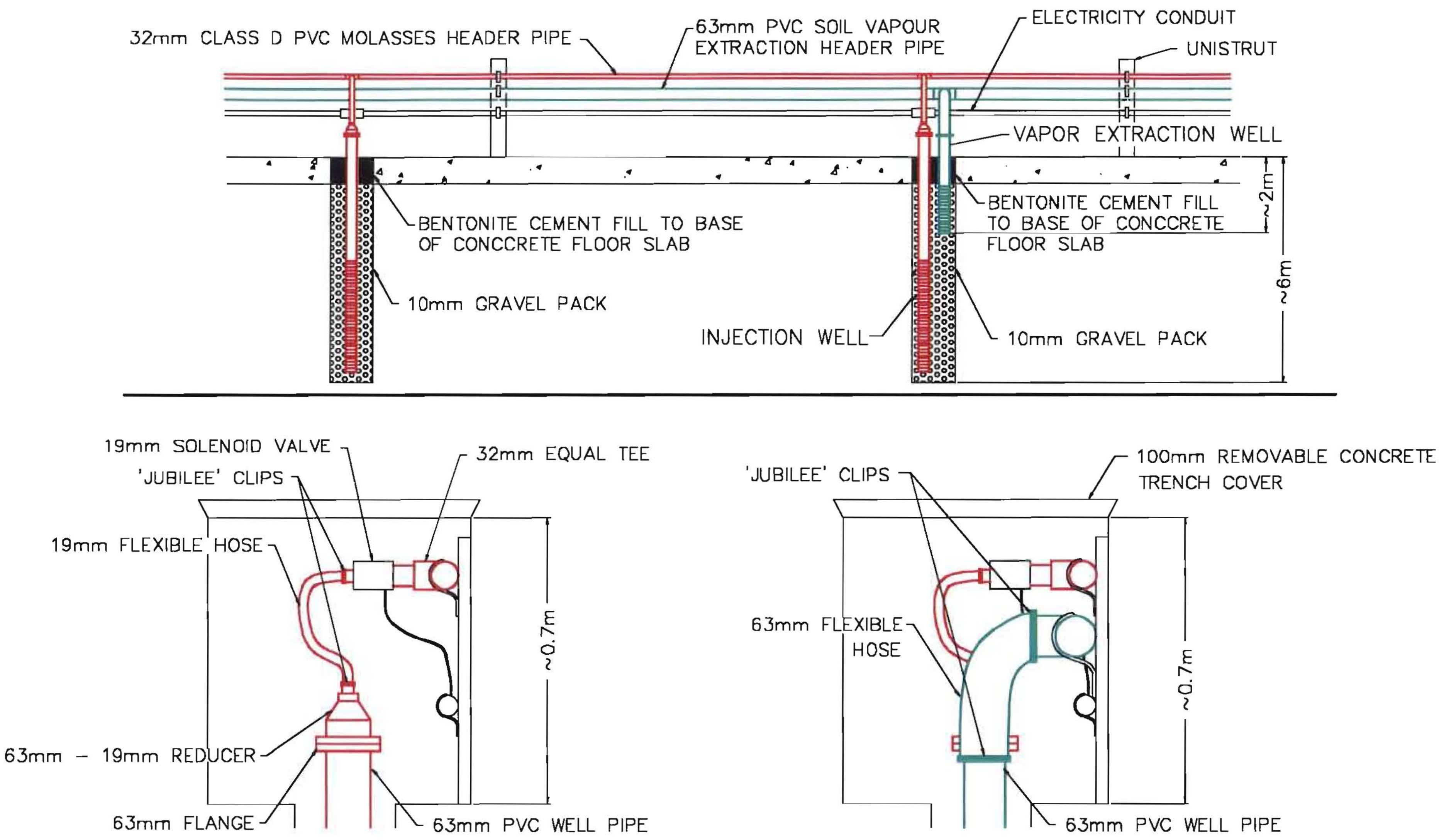


Figure 3 System Layout: Plan View



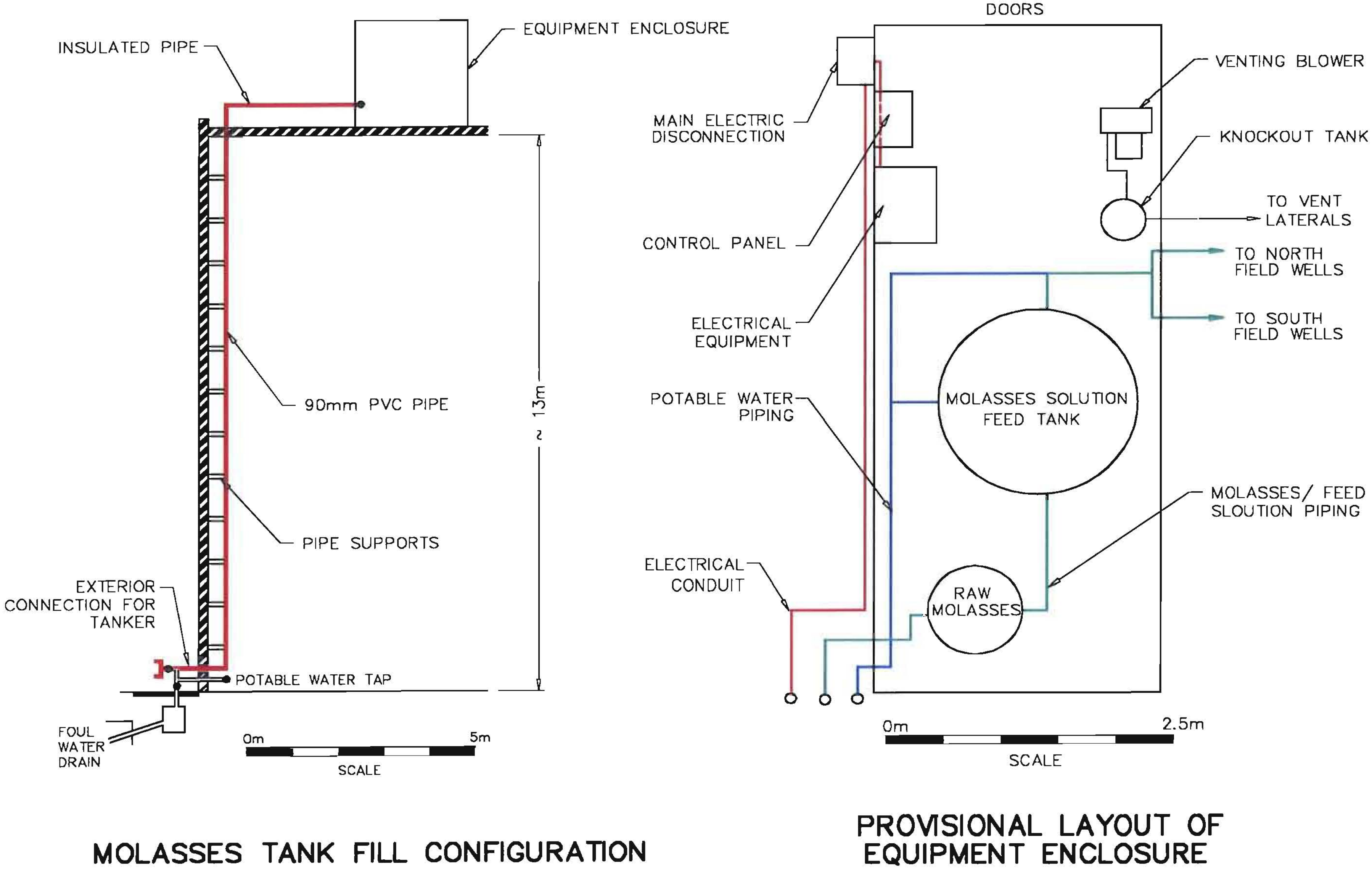
**MOLASSES INJECTION WELL**

**SOIL VAPOUR EXTRACTION WELL**

Figure 4 Molasses Injection - Injection Well Detail

Picture 1 Low Profile Injection Trench

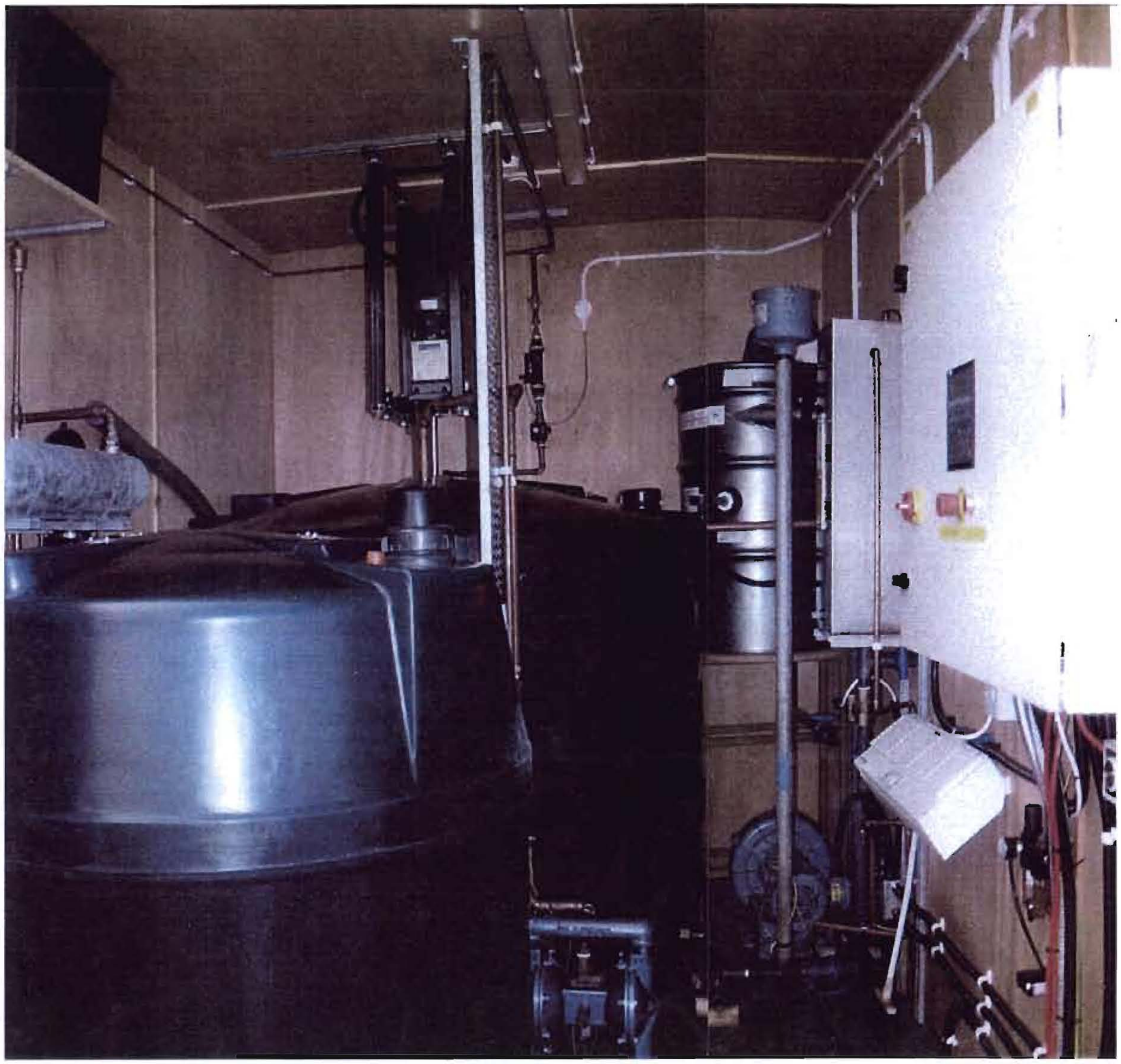
Picture 2 Roof Mounted Injection Building



MOLASSES TANK FILL CONFIGURATION

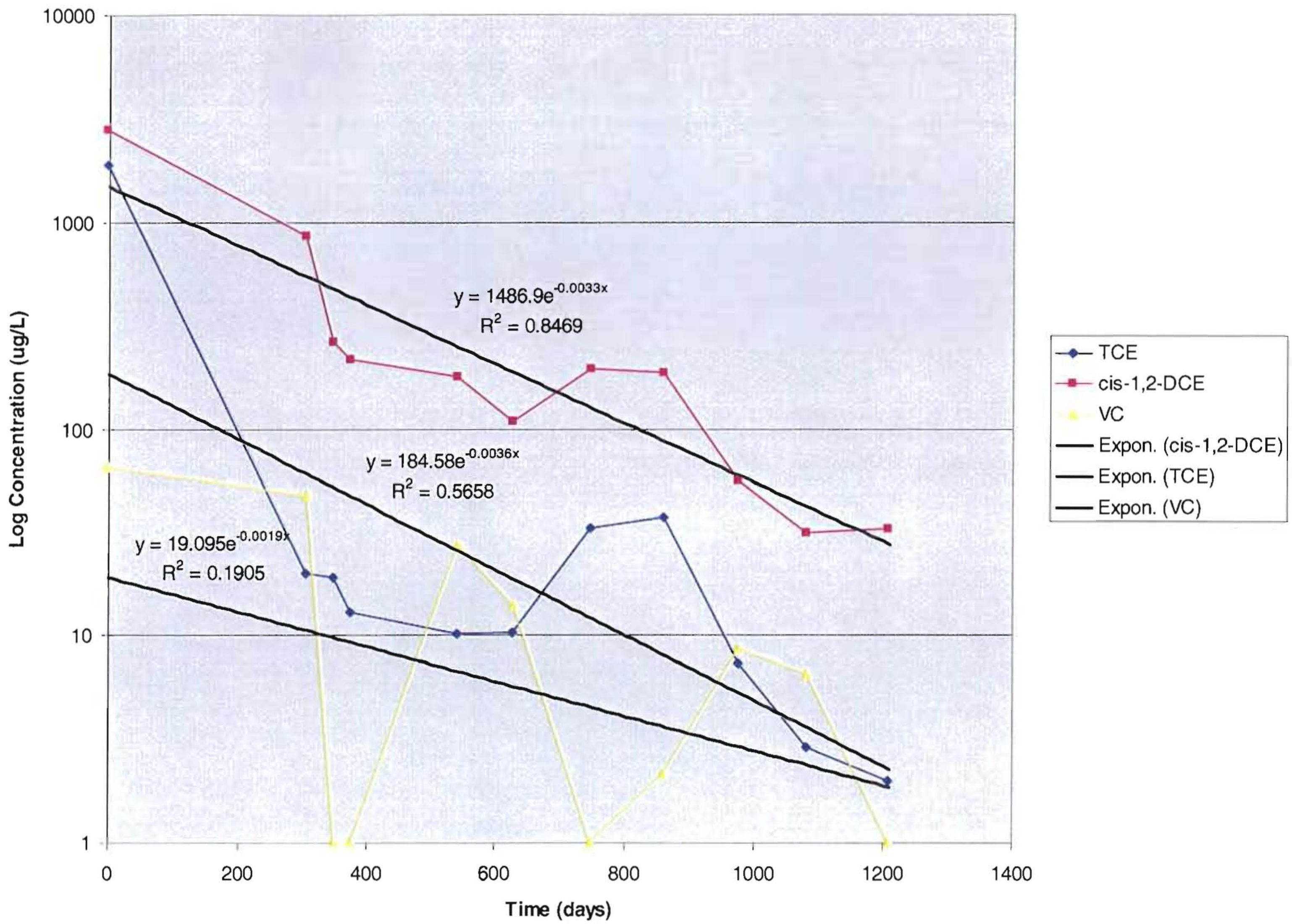
PROVISIONAL LAYOUT OF EQUIPMENT ENCLOSURE

Figure 5: Molasses Injection - Mixing and Control System



Picture 3 Injection Building (Interior)

# Figure 6: CVOC Trends and Rate Calculations for MW-4



# SITE 5

### Site 5 –Dry Cleaner Wisconsin

ARCADIS utilized its patented in-situ enhanced reductive dechlorination (ERD) process to treat groundwater impacted with tetrachloroethylene (PCE) and its daughter products at a former dry cleaning facility located in Wisconsin. A dilute molasses solution was utilized as the electron donor (Lenzo, 2000; Suthersan, 2000). The use of a full-scale ERD approach at this site resulted in complete PCE degradation and conversion to innocuous end products in less than a two-year time frame.

Prior to implementing the ERD process, the source of PCE that caused site groundwater contamination at the former dry cleaning facility was effectively removed through soil excavation and off-site disposal. Twenty months after implementing the ERD process, PCE concentrations within the plume decreased from pre-remediation levels of approximately 1,500 to 4,000 micrograms per liter (µg/L) to non-detectable levels. As expected, there was a corresponding increase in cis-1,2-dichlorethylene (DCE) and vinyl chloride (VC) concentrations, which occurred in conjunction with the decrease in PCE concentrations. The corresponding build-up of DCE and vinyl chloride peaked at approximately 6 and 14 months, respectively, after initiating the ERD process. The DCE and vinyl chloride levels then dropped sharply over the next 6 months. Ethene and ethane levels increased over two orders of magnitude (exceeding 400 ug/L) in conjunction with the decreasing concentrations of DCE and VC. Based on stoichiometric relationships, it is estimated that more than 90% of the PCE was degraded to ethene and ethane within the 20-month period. Regulatory approval for site closure was received in January 2001, less than 2 ½ years after initiating the ERD process. This expedited remediation time frame demonstrates the importance of source removal and proper implementation of the ERD process.

### Background

Prior to 1998, the former dry cleaning facility was part of a dilapidated retail center (Picture 1). This property was redeveloped concurrently with the site remediation activities and is currently a successful retail shopping center (Picture 2). Contamination at the site resulted from historic releases of PCE, a common dry cleaning solvent, from a dry cleaning facility that operated within the former shopping mall. The location of the former dry cleaners is presented on Figure 1.

A soil remediation program was completed in August 1998 and involved the excavation and off-site disposal of approximately 3,125 tons ($2.8\times10^6$ kilograms) of PCE-impacted soils. The excavation extended down to the water table, which was even with the top of a saturated sand seam at a depth of approximately 14 feet (4.27 meters) below initial grade. In order to maintain suitable conditions for backfilling and to achieve additional contaminant mass removal, provisions were included for the temporary recovery of groundwater from the base of the excavation. Approximately 88,375 gallons (334,499 liters) of water were pumped from the excavation and discharged to the sanitary sewer in August 1998. It is estimated that approximately 25,000 gallons (94,625 liters) of this volume was attributable to precipitation or surface water run-in that accumulated in the excavation, and the remainder was groundwater recovered from the sand seam that was penetrated by the deep excavation.

The lateral and vertical extent of affected groundwater was defined, and was approximately 30,000 square feet (2,787 square meters) in plan size, extending to a depth of approximately 20 feet (6.10 meters) below grade. The investigation results suggested that the affected groundwater had spread laterally from the source area primarily through a 2 to 5 feet (0.61 to 1.52 meters) thick silt and sand seam that is approximately 13 to 18 feet (3.96 to 5.49 meters) below grade. Within this seam, the extent of impacted groundwater was estimated to be 150 feet (45.72 meters) in width by 200 feet (60.96 meters) in length. A representative geologic cross section is presented in Figure 2.

### The ARCADIS Approach

The groundwater remediation process involved the periodic injection of an organic carbon (molasses) solution to enhance the reductive dechlorination of the chlorinated solvents present in site groundwater (i.e., an in-situ bioremediation process). By injecting an organic carbon source, anaerobic and strong reducing conditions were created within the in-situ reaction zone. These conditions created a more suitable environment for the degrading microorganisms to promote both the desorption of the PCE from the aquifer matrix and the ERD (i.e., biodegradation) of the PCE (Payne et al, 2001). The dilute molasses solution was injected to create a reactive zone throughout the entire area of impacted groundwater.

## MATERIALS AND METHODS

Following completion of the soil excavation activities, the groundwater remediation program was implemented at the site. An initial injection event was conducted in August and September 1998, using 182 temporary Geoprobe® injection points. The Geoprobes® were advanced in a grid-like pattern across the groundwater target area. The spacing between each Geoprobe® was approximately 10 feet (3.05 meters). The borings were advanced to intersect the sand seam ranging from 13 to 18 feet (3.96 to 5.49 meters) below ground surface. The temporary injection wells were constructed of 1-inch (2.54-centimeter) diameter polyvinyl chloride (PVC) pipe for the well screen and riser. Bentonite pellets were used to seal the temporary wells.

Edible blackstrap molasses was used for the initial injection. The edible blackstrap molasses is approximately 47% carbohydrates by weight. The molasses solution was mixed in a plastic tank on site using potable water. Approximately 15 to 25 gallons (56.78 to 94.63 liters) of the dilute molasses solution [the dilution ratio was 25 gallons (94.63 liters) of water to each gallon (3.79 liters) of molasses] were injected into each temporary well using a grout pump. Approximately 3,190 gallons (12,074 liters) of the dilute molasses solution were injected into the temporary injection points over 11 days.

A permanent injection system was installed concurrently with the initial injection event. Twelve fixed injection wells were installed at the site using conventional hollow-stem auger drilling techniques [4¼-inch (0.11 meter) inside diameter augers]. The locations of these wells are shown on Figure 1. The fixed injection wells consisted of a 2-inch (5.08-centimeter) diameter Schedule 40 PVC riser with a 2-inch (5.08-centimeter) diameter Schedule 40 PVC well screen. Each injection well screen consisted of a 5-foot (1.5 meter) length of 0.010-inch (0.25 millimeters) slotted well screen placed to intersect the sand seam approximately 13 to 18 (4 to 5.5 meters) feet below ground surface. The annular space between the well screen and borehole was filled with a clean silica sand filter pack from the bottom of the boring to one foot above the top of the screen. Approximately 1 foot (0.3 meters) of fine sand was placed above the filter pack, and a bentonite seal was installed to the depth where the conveyance piping would be connected to the well. To facilitate the redevelopment at the site, the injection wells were cut off approximately 6 feet (1.8 meters) below ground surface and connected to 1-inch (2.54 centimeter) high-density polyethylene (HDPE) buried conveyance piping.

A network of 1-inch (2.54-centimeter) HDPE conveyance piping was installed below grade between the injection equipment building and the permanent injection wells. The remedial system equipment was housed within a small heated and insulated building. The remedial equipment included a 250-gallon (946 liters) plastic mix tank, a piping manifold, and 1/3 horsepower (0.25 kilowatt) rotary gear pump.

After the fixed injection system was installed, four additional injection events were completed at the site. The molasses solution was added to the mix tank and pumped through the manifold to the injection wells at a dilution ratio of 25 gallons (94.63 liters) of water to each gallon (3.75 liters) of molasses. The molasses used for the permanent injection wells was a low-sulfur, cane juice molasses that contained approximately 66% carbohydrates by weight. A total of 2,985 gallons (11,298 liters) of the molasses solution was injected into the aquifer through the permanent injection wells during the four injection events completed over a six-month period from March 1999 to September 1999.

The quantity of the dilute molasses solution injected into the aquifer and the timing of each event was determined based on changes in biodegradation indicator parameters and the rate of reductive dechlorination determined from the groundwater monitoring data collected over time from the site monitoring well network. The optimum values for groundwater indicator parameters for the ERD process included an oxidation-reduction potential of less than –200 millivolts, total organic carbon in the range of

25-100 milligrams per liter (mg/L), and a pH above 5. Due to site redevelopment activities occurring concurrently with the groundwater remediation, post-injection groundwater monitoring did not begin until 6 months following the initial injection event. The site monitoring well network consisted of four monitoring wells within the limits of the plume and eight monitoring wells located outside of the plume. Figure 1 shows the locations of the monitoring wells.

## RESULTS

Six rounds of groundwater sampling were completed from February 1999 to April 2000 following implementation of groundwater remediation at the site. Over the 20-month period following completion of soil remediation activities and the initial carbon injection event (August 1998), PCE concentrations within the plume decreased to non-detectable levels (April 2000). As expected, a temporary increase in DCE and vinyl chloride concentrations occurred in conjunction with the decrease in PCE concentrations. The corresponding build-up of DCE and vinyl chloride peaked at approximately 6 and 14 months, respectively, after initiating the ERD process. The DCE and vinyl chloride levels then dropped sharply over the next 6 months. Figures 3 and 4 illustrate the contaminant concentration changes over time for two of the monitoring wells located within the plume.

A buildup of the non-toxic, innocuous end products of the reductive dechlorination process (e.g., ethene, ethane, carbon dioxide) indicated that the source PCE was being completely transformed. The monitoring data collected indicated significant production of ethene and ethane within the groundwater plume. Ethene and ethane concentrations in the four monitoring wells within the plume were detected approximately one to two orders of magnitude higher than the ethene and ethane levels measured in the monitoring wells located along the fringe of the plume. This was clear evidence that the reductive dechlorination process was going to completion.

Based on the use of first-order degradation kinetics, the biodegradation rates for the chlorinated constituents at the site can be determined (U.S. EPA, 1998). Table 1 lists the average site-specific biodegradation rates determined from the collected data for each of the monitoring wells within the groundwater plume. The site-specific biodegradation rates are approximately two to eight times higher than average published biodegradation rates under natural conditions (U.S. EPA, 1998). This demonstrates that the ERD process can greatly accelerate biodegradation rates. Note that the total molasses solution injected was only approximately 2 percent of the total volume of groundwater in the target area, indicating that dilution effects on the observed rates were minimal.

**TABLE 1. Calculated Site Biodegradation Rates (day$^{-1}$)**

| | Monitoring Well | | | |
|---|---|---|---|---|
| **Compound** | **MW-13** | **MW-14** | **MW-15** | **MW-16** |
| **PCE** | Not applicable | 0.027 | Not applicable | 0.021 |
| **TCE** | 0.011 | 0.005 | Not applicable | 0.023 |
| **DCE** | 0.010 | 0.004 | 0.011 | 0.017 |
| **VC** | 0.015 | 0.003 | 0.011 | 0.018 |

Changes in the molar concentration over time of the parent compound (PCE) and its daughter products (TCE, DCE, VC, ethene, ethane) are presented on Figures 5 and 6 for two of the monitoring wells located within the plume. This data illustrate that within 6 months of implementing the ERD process, over 90% of the PCE was degraded to DCE. In addition, within 20 months of initiating the ERD process, over 90% of the PCE in the groundwater plume was degraded to ethene and ethane.

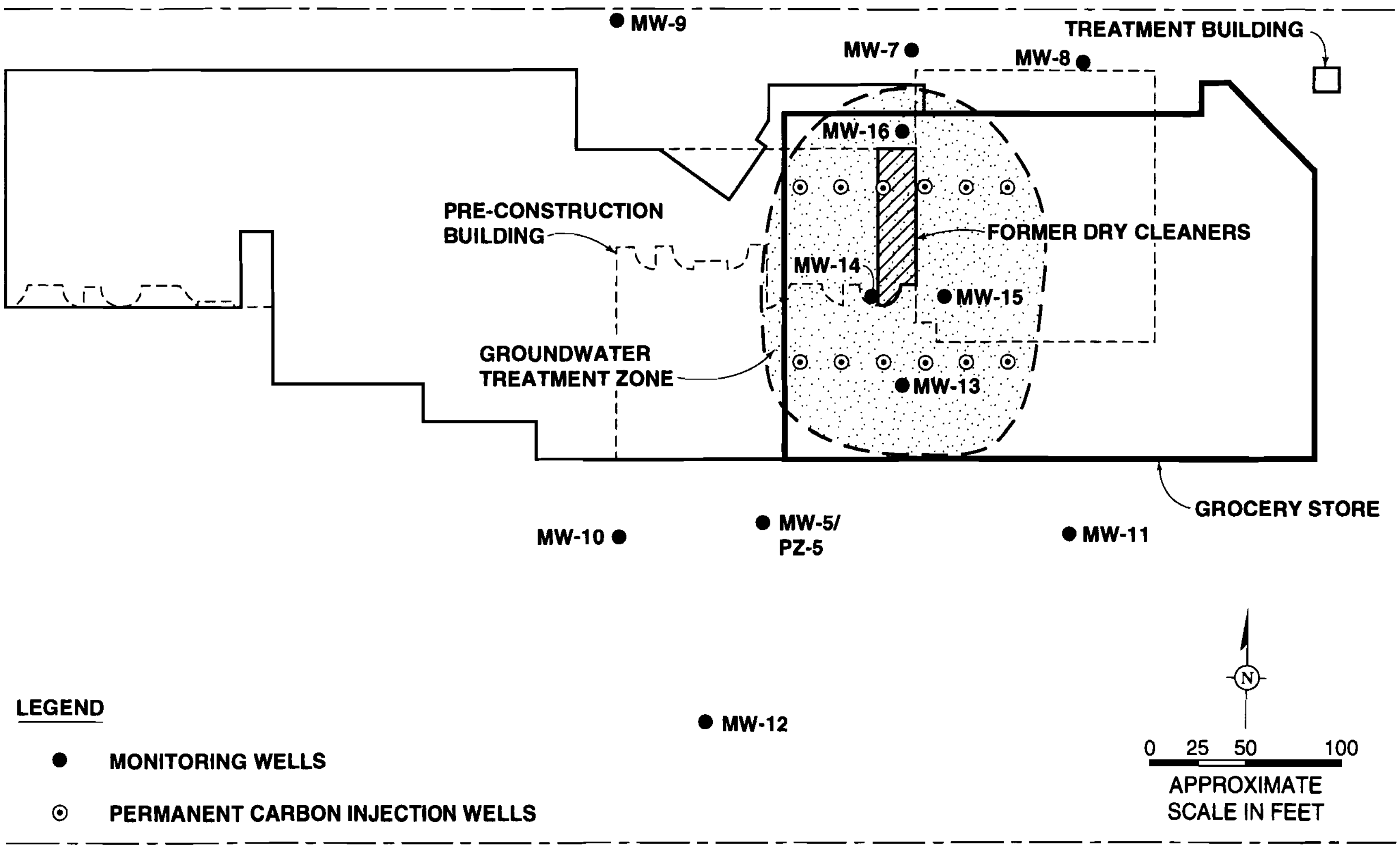
## CONCLUSION

This project demonstrates that source removal and proper implementation of the ERD process can greatly expedite the remediation time frame for PCE contaminated groundwater. Twenty months after implementing the ERD process, PCE concentrations within the plume decreased from pre-remediation levels of approximately 1,500 to 4,000 micrograms per liter (µg/L) to non-detectable levels. Based on stoichiometric relationships, it is estimated that more than 90% of the PCE was degraded to ethene and ethane within the 20-month period. Regulatory approval for site closure was received in January 2001, less than 2 ½ years after initiating the ERD process.

Picture 1 Former Dry Cleaning Facility (Pre Redevelopment)

Picture 2 Post Treatment, Redeveloped Property

# Figure 1 Site Layout



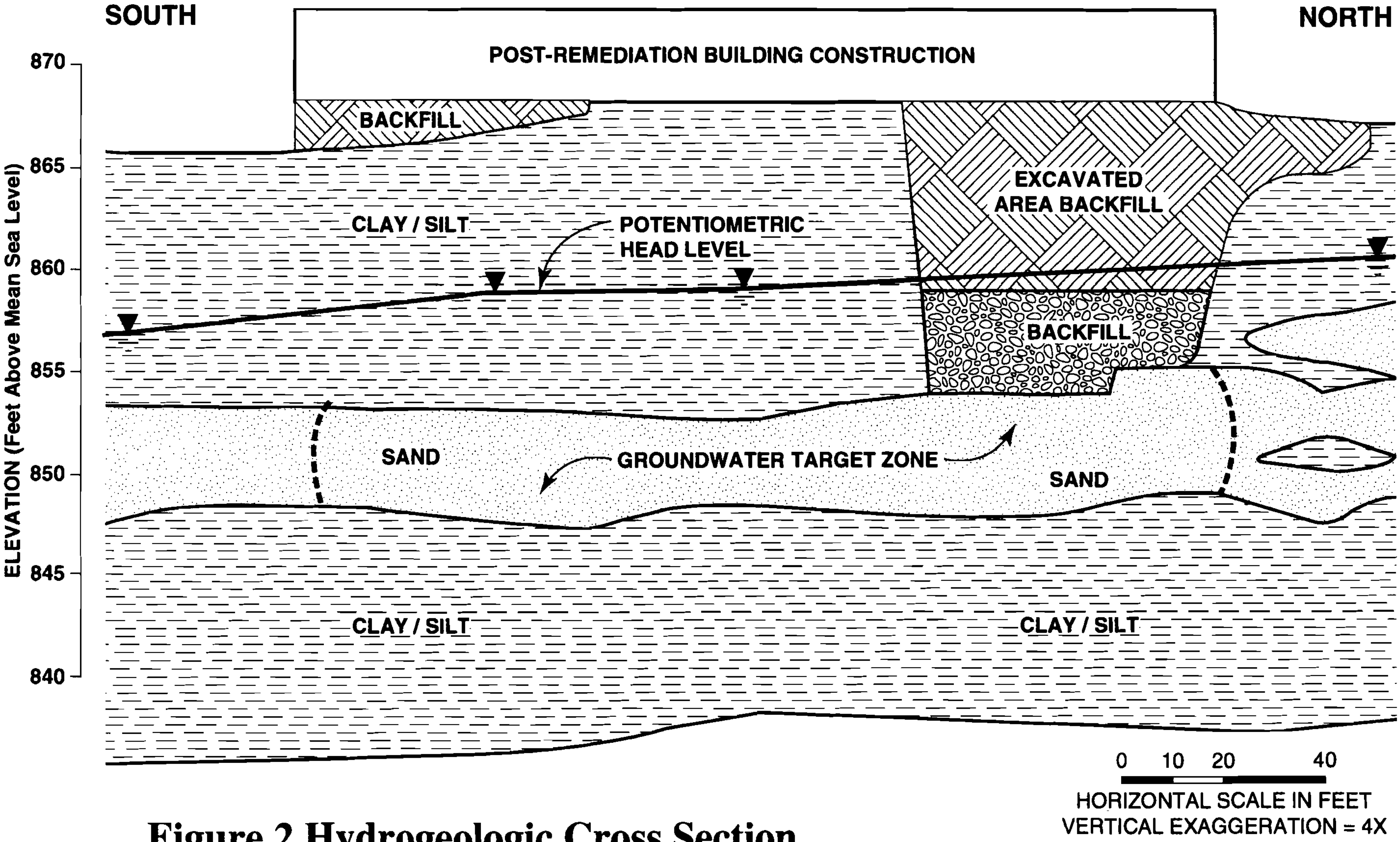
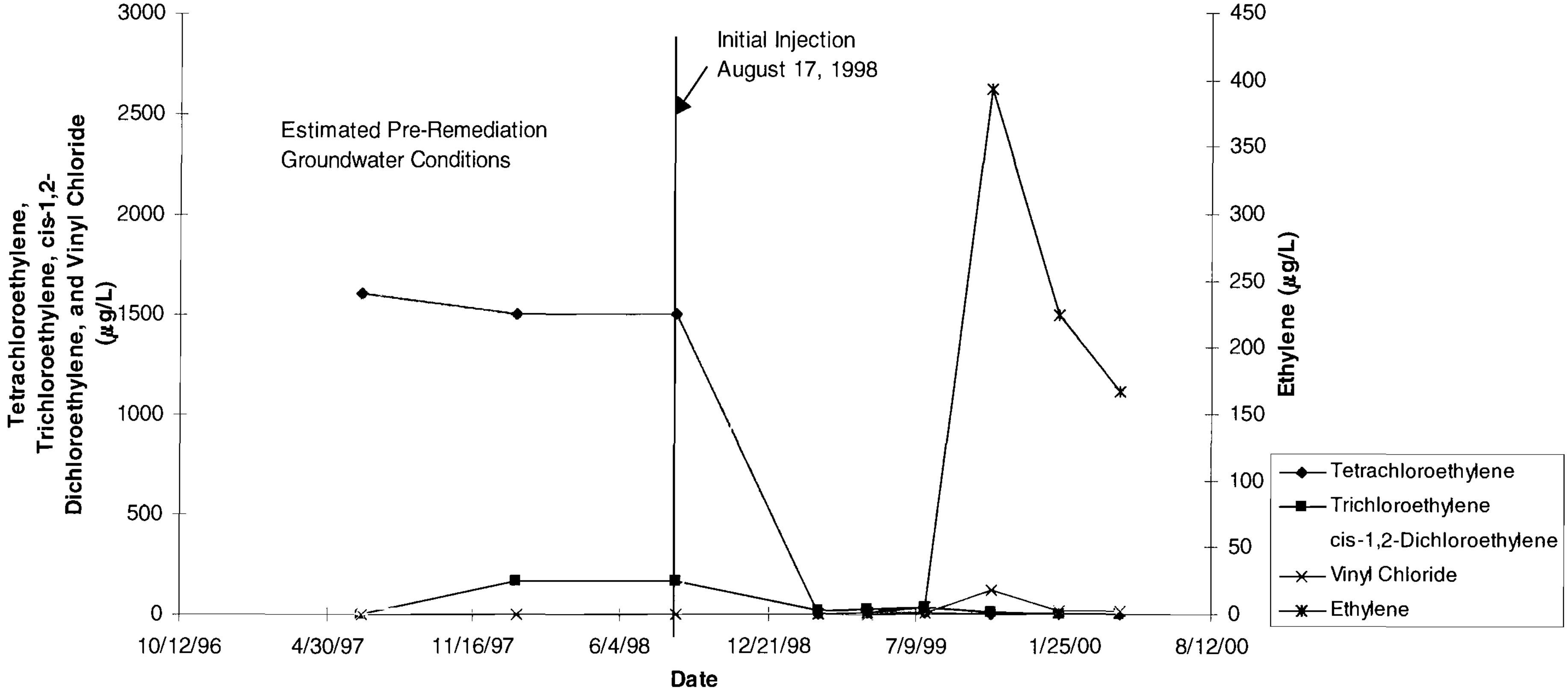


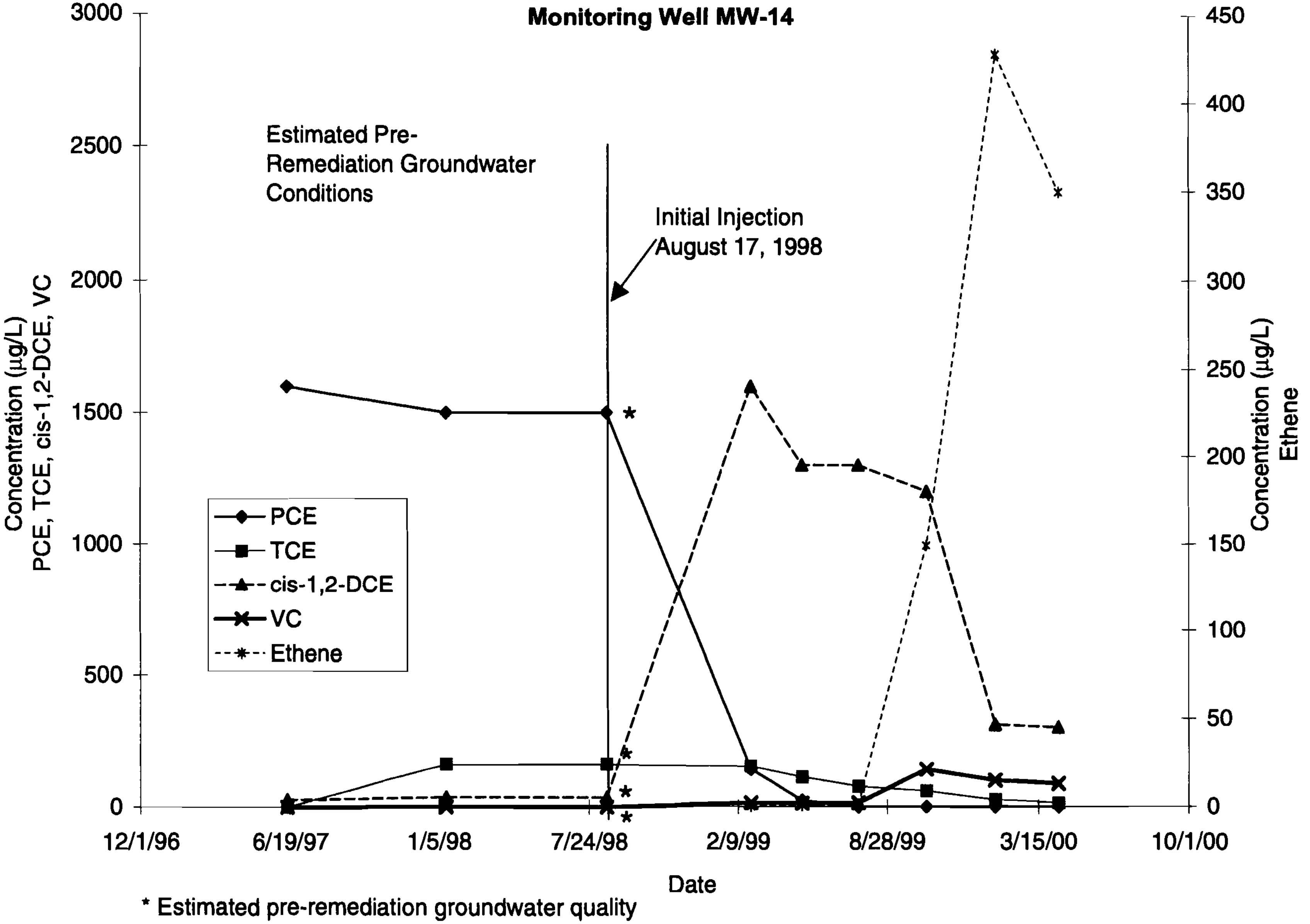
Figure 2 Hydrogeologic Cross Section

# Figure 3 Monitoring Well MW-13
# Groundwater Contaminant Concentrations Versus Time



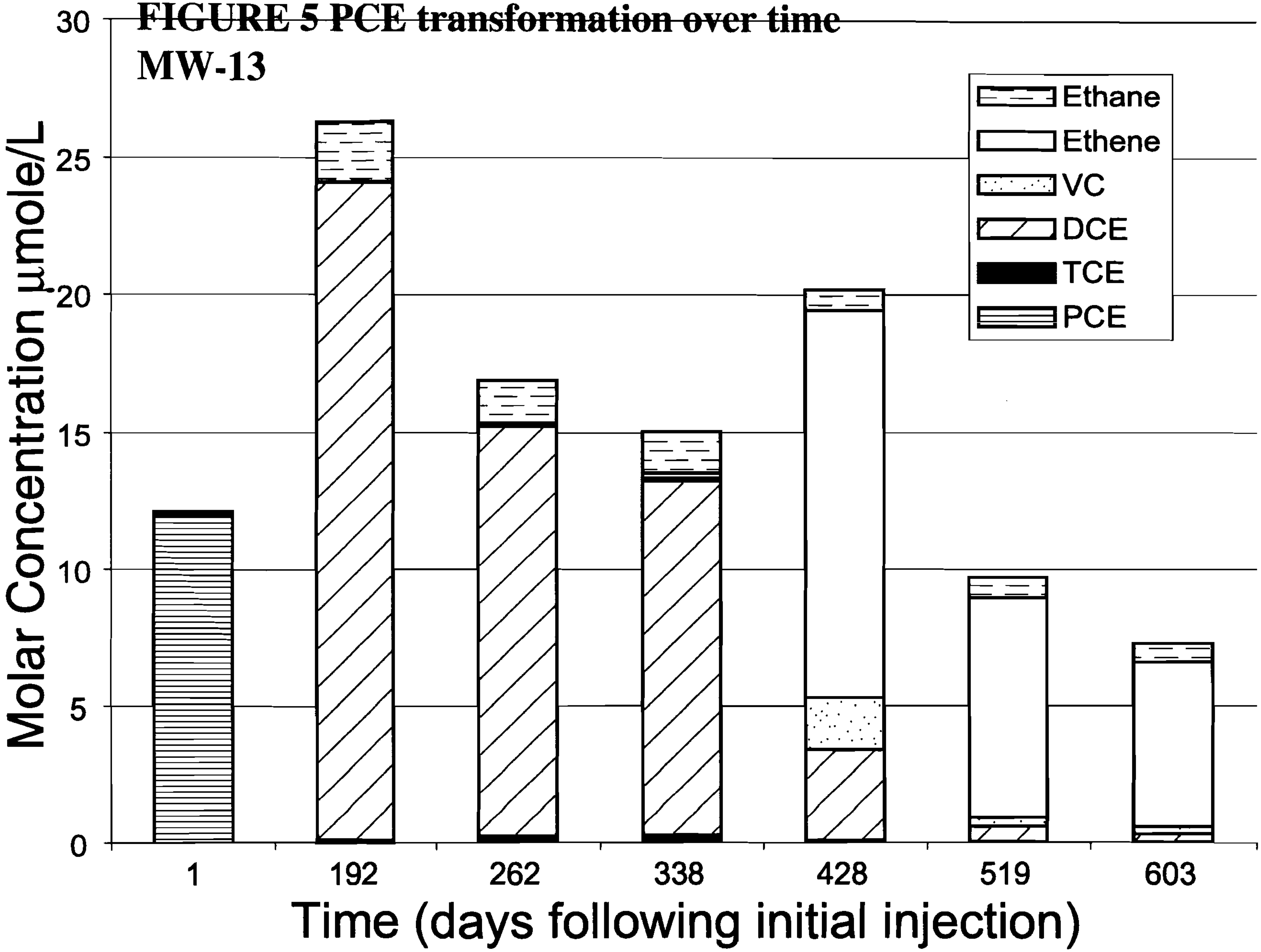
**PCE→TCE→1,2-DCE→Vinyl Chloride→Ethene→Ethane→$CO_2$+**

# Figure 4



* Estimated pre-remediation groundwater quality

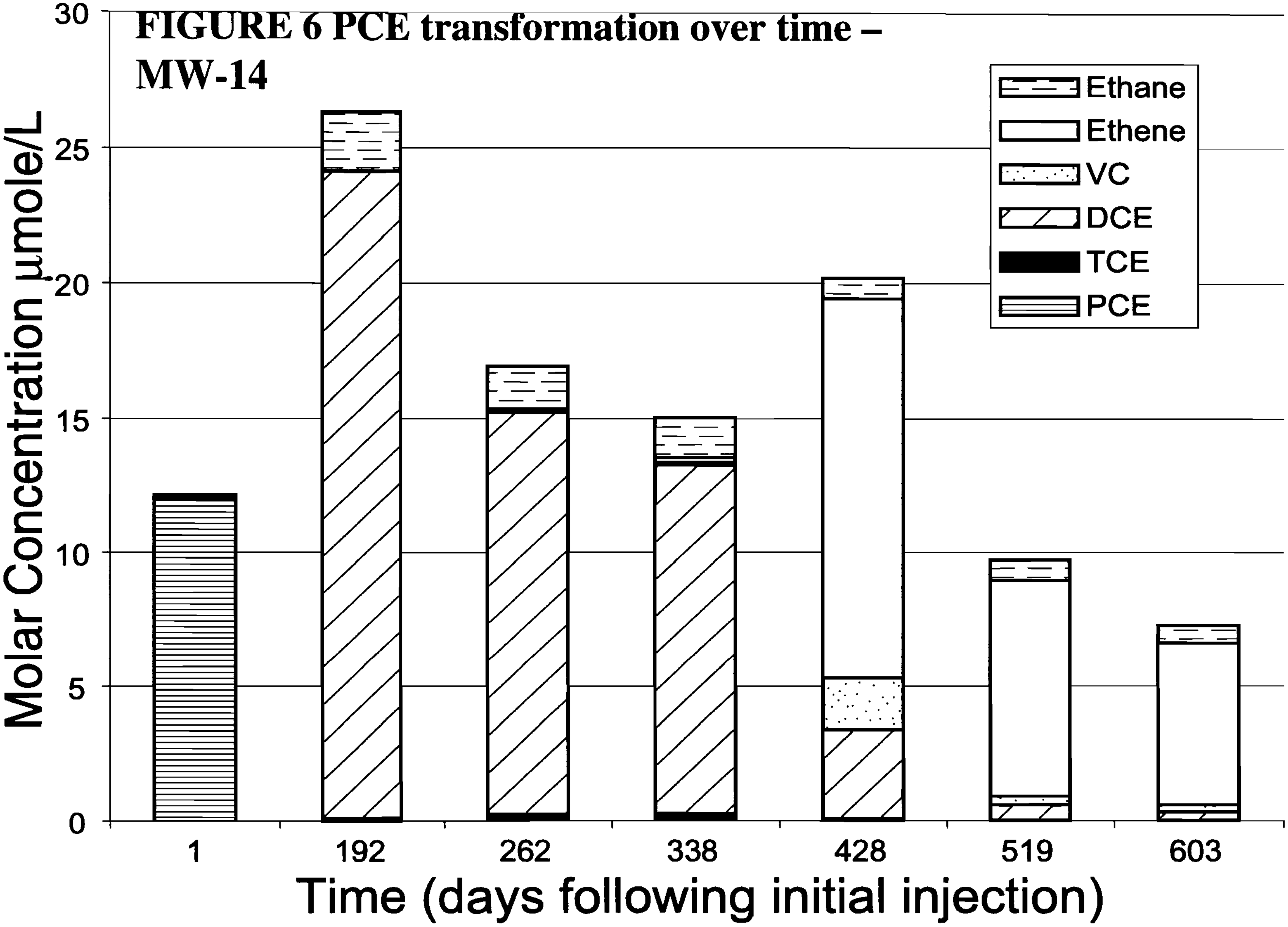
# FIGURE 5 PCE transformation over time MW-13



PCE → TCE → DCE → VC → Ethene → Ethane

▤ ■ ▨ ░ □ ▤

## FIGURE 6 PCE transformation over time – MW-14



PCE → TCE → DCE → VC → Ethene → Ethane

# SITE 6

# EXPLANATION OF SIGNIFICANT DIFFERENCES

## COLESVILLE MUNICIPAL LANDFILL SUPERFUND SITE

Colesville Township
Broome County, New York

EPA
Region 2

September 2000

## INTRODUCTION

**In accordance with the Comprehensive Environmental Response, Compensation, and Liability Act of 1980, as amended ("CERCLA"), 42 U.S.C. §9617(c), and Section 300.435(c)(2)(i) of the National Oil and Hazardous Substances Pollution Contingency Plan ("NCP"), if after the Environmental Protection Agency ("EPA") selects a remedial action, there is a significant change with respect to that action, an explanation of the significant differences ("ESD") and the reasons such changes were made must be published.**

EPA issued a March 1991 Record of Decision ("ROD") for the Colesville Landfill site that called for, among other things, capping the landfill, collecting and treating contaminated groundwater, and providing a new water supply system for the affected residents.

Installation of the landfill cap was completed in 1995. The provision of a new water supply system is on hold pending the efforts of the County to purchase the affected properties. Based upon the results of field tests and post-capping groundwater sampling, it was determined that the groundwater extraction system called for in the ROD, by itself, is not likely to be an effective means of remediating the groundwater. Therefore, an enhancement of the remedy will be employed to restore the groundwater to federal and state standards within a reasonable time frame.

**This ESD will become part of the Administrative Record file for the site. The entire Administrative Record for the site, which includes the remedial investigation and feasibility study ("RI/FS") report, ROD, design reports, a post-ROD investigation and evaluation of alternative technologies report, and other relevant documents, are available for public review at the following locations:**

Town of Colesville Town Hall
Harpursville, NY 13787

**New York State Department of**
**Environmental Conservation**
**50 Wolf Road, Room 222**
**Albany, NY 12233-7010**

**and**

**U.S. Environmental Protection Agency**
**290 Broadway, 18th floor**
**New York, New York 10007**

**The changes to the selected remedy are not considered by EPA or the New York State Department of Environmental Conservation ("NYSDEC") to be a fundamental alteration of the remedy selected in the ROD. The remedy modification maintains the protectiveness of the groundwater action with respect to human health and the environment, increases the cost-effectiveness of the action, and complies with federal and state requirements that were identified in the ROD.**

## SUMMARY OF SITE HISTORY, CONTAMINATION PROBLEMS, AND SELECTED REMEDY

**Waste disposal operations at the landfill commenced in 1969. The landfill was owned and operated by the Town of Colesville between 1969 and 1971. Broome County purchased the landfill in 1971, operating it until it closed in 1984.**

**The landfill was primarily used for the disposal of municipal solid waste, although drummed industrial wastes from various sources were also disposed of between 1973 and 1975. The drums were either buried intact or punctured and crushed prior to burial.**

**In 1983, samples collected by the Broome County Health Department from residential wells in the vicinity of the site indicated that the landfill was contaminating the groundwater in the vicinity of the site. The sample results prompted the Broome County Department of Public Works to install carbon filters on the affected residences, to initiate a residential well monitoring program, and to perform further investigation of the landfill in 1983 and 1984. These investigations showed elevated levels of a number of volatile organic compounds ("VOCs") in the groundwater.**

**The site was proposed for inclusion on the Superfund National Priorities List ("NPL") in October 1984 and was listed on the NPL in June 1986. NYSDEC was designated the lead agency for this site.**

**In 1990, an RI/FS was completed by Broome County and GAF Corporation, potentially responsible parties ("PRPs") identified for the site, pursuant to an Order on**

Consent (Index No. T010687) issued by NYSDEC (the "State Order").

In 1991, based upon the results of the RI/FS, EPA issued a ROD, selecting a remedy for the site. The selected remedy included, among other things, the installation of a multimedia cap on the landfill, the collection and treatment of contaminated groundwater, and the provision of new deep wells for six affected residences located in the vicinity of the site.

Pursuant to the State Order, the PRPs began the engineering design of the selected remedy in 1991. In 1994, the PRPs completed the engineering design for the capping of the landfill and completed the capping of the landfill in 1995.

An alternate water supply well design was approved by the State in 1995. The implementation of the design has, however, been delayed pending Broome County's purchase of the six affected residences and the placement of deed restrictions preventing the installation and use of groundwater wells on the properties, so that there will be no drinking water receptors. To date, the County has purchased three of the properties and is trying to purchase the remaining properties. Of the three remaining properties, one is abandoned and two have deep bedrock wells, which have always tested clean. The County is, however, maintaining carbon filters on the two bedrock wells. One of the remaining properties also has a shallow well which services a fishing camp located on the property. Sample results from this well indicated the presence of low levels of VOCs and bacteria. The County is providing the fishing camp residents with bottled water. It is anticipated that the County will either purchase the remaining properties or install new water supply wells by the end of 2000. If all of the affected properties are purchased and deed restrictions preventing the installation and use of groundwater wells on the properties are implemented, EPA will consider modifying the remedy to eliminate the need to install the alternate water supply well design called for in the ROD.

## DESCRIPTION OF SIGNIFICANT DIFFERENCES AND THE REASONS FOR THOSE DIFFERENCES

Based upon design-related aquifer tests conducted at the site, it was determined that extracting contaminated groundwater from beneath the landfill, as called for in the ROD, would not likely be an effective means of remediating the groundwater at the source in a reasonable time frame. Specifically, the aquifer tests determined that the aquifer has a low permeability, which would severely limit the area of influence of the extraction wells and would allow the groundwater to be pumped at only a very low rate (0.25 to 0.5 gallon per minute). Such conditions would necessitate the installation of an inordinate number of extraction wells. This conclusion led to an evaluation of alternative groundwater technologies and the performance of a pilot-scale study to evaluate the effectiveness of one of the more promising technologies. This pilot-scale study involved injecting the impacted groundwater with molasses, which accelerated the microbial degradation of the VOCs in the groundwater[1]. Based upon the results of the pilot study, which showed a significant decline in VOC concentrations, it was concluded that this technology, in combination with the installation of downgradient extraction wells, as called for in the ROD, offers the most technically feasible approach to restoring groundwater quality in a reasonable time frame[2].

A final groundwater remediation design, using this technology in combination with a downgradient groundwater extraction and treatment system, was approved by NYSDEC on August 24, 2000. It is anticipated that construction will commence in late September 2000.

## STATE AGENCY COMMENTS

NYSDEC supports the change to the remedy.

## AFFIRMATION OF STATUTORY DETERMINATIONS

EPA and NYSDEC believe that the modified remedy is as protective as the ROD remedy with respect to human health and the environment, increases the cost-effectiveness of the action, and complies with federal and state requirements that are applicable or relevant and appropriate to this remedial action. In addition, the remedy continues to utilize permanent solutions and alternative treatment technologies to the maximum extent practicable for this site.

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[1] The technical name of this process is "enhanced reductive dechlorination." Under this process, microbes remove the chlorine from the VOCs, allowing the compounds to further degrade into carbon dioxide and water.

[2] Based upon preliminary modeling results, it is estimated that it will take 7 to 10 years to remediate the aquifer downgradient of the landfill using the molasses technology in combination with the installation of downgradient extraction wells, as compared to an estimated 65 years for site-wide groundwater extraction and treatment.

## PUBLIC PARTICIPATION ACTIVITIES

*EPA and NYSDEC are making this ESD and supporting information available to the public in the Administrative Record. EPA and NYSDEC invite comments or questions related to this ESD. Comments or questions should be directed to:*

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U.S. Environmental Protection Agency
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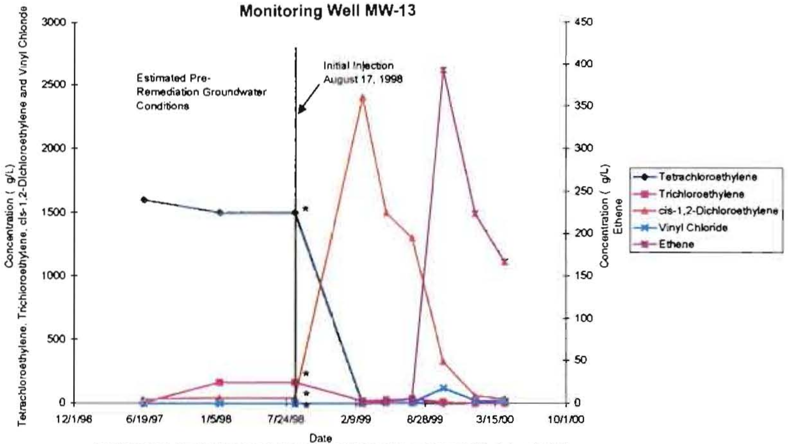
New York, NY 10007-1866

Telephone: **(212) 637-4266**
Telefax: (212) 637-3966
E-mail: jacob.george@epa.gov

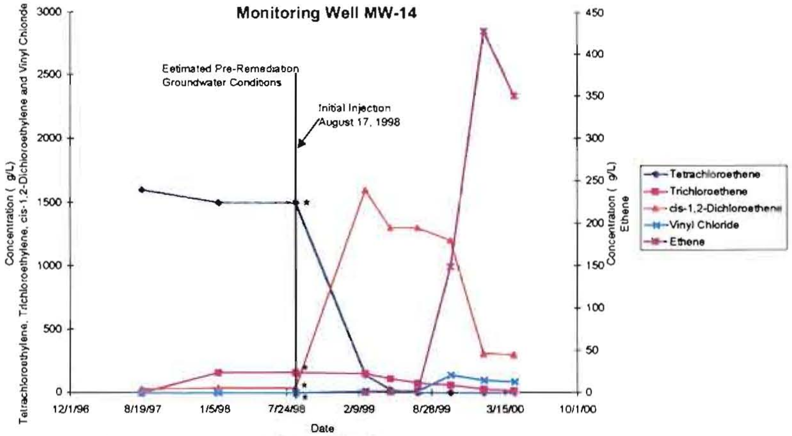
ARCADIS

# SITE 7

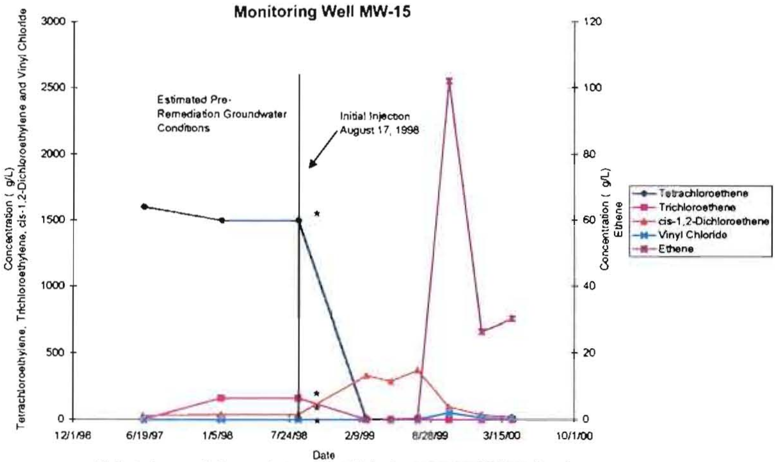
DRAFTER: ELS | APPROVED | CHECKED: JC | DRAWING: GRAPHS_4.AI | FILE NO.: GRAPHICS | PN. MEQUONPI\WI0679\WORKPLAN | DWG DATE: 03AUG00



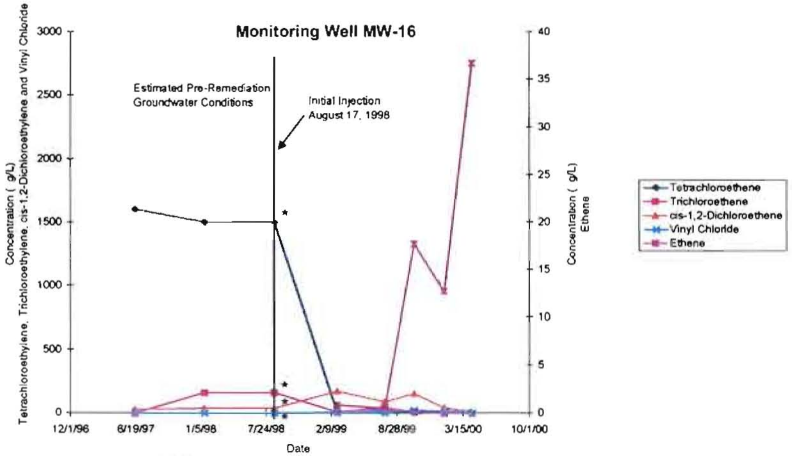
* Estimated pre-remediation groundwater quality at this location is represented by data collected from Monitoring Well MW-3. Monitoring Well MW-13 was installed February 11, 1999.



* Estimated pre-remediation groundwater quality at this location is represented by data collected from Monitoring Well MW-3. Monitoring Well MW-14 was installed February 11, 1999



* Estimated pre-remediation groundwater quality at this location is represented by data collected from Monitoring Well MW-3. Monitoring Well MW-15 was installed February 11, 1999.



* Estimated pre-remediation groundwater quality at this location is represented by data collected from Monitoring Well MW-3. Monitoring Well MW-16 was installed February 12, 1999.

ARCADIS
GERAGHTY & MILLER

**GROUNDWATER REMEDIATION PERFORMANCE MONITORING DATA**

WASHINGTON SQUARE MALL PROPERTY
GERMANTOWN, WISCONSIN

FIGURE

**13**